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APPLICATION

OF

SOME GENERAL REACTIONS

TO INVESTIGATIONS IN

ORGANIC CHEMISTRY.

BY

Dr. LASSAR-COHN,

Professor of Organic Chemistry at the University of Königsberg.

AUTHORIZED TRANSLATION

BY

J. BISHOP TINGLE, Ph.D. (Munich), F.C.S.,

Johns Hopkins University.

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TRANSLATOR'S PREFACE.

PROBABLY every student of organic chemistry, at some period of his career, becomes more or less overpowered by the immense mass of detail which he encounters, and it is only as he is able to apprehend the fundamental principles and generalizations underlying these facts that he can emerge from the labyrinth. The topics considered in this latest little book of Professor Lassar-Cohn are of considerable importance, and have hitherto failed to receive adequate treatment in other works. It is hoped that the volume may prove useful to students who are threatened with the difficulty mentioned above, and also that it may appeal to teachers and others engaged in research work, both on account of the broad, suggestive discussion of the subjects which it embraces, and also because it includes mention of numerous themes which demand investigation.

J. BISHOP TINGLE.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
October 1904.

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AUTHOR'S PREFACE.

A SURVEY of the enormous number of investigations which are constantly appearing in the domain of organic chemistry reveals the fact that, although their theoretical portions are based, in the most severely logical fashion, on the tetravalency of the carbon atom, the technique of the research is essentially empirical. An intimate connection with organic investigation, extending over many years, has convinced me of the availability of certain general principles in the practical part of the work; they are partly theoretical, partly practical in their nature, and *their application to the praxis of organic research is capable of affording general help and improvement in an enormously large number of cases*. In this book I have presented all the material bearing on the subject which I have accumulated.

LASSAR-COHN.

KÖNIGSBERG I. PR.,
July 1904.

CONTENTS.

CHAPTER I.

PAGE
INTRODUCTORY. FIXATION OF LABILE HYDROGEN ATOMS.... 1

CHAPTER II.

MODIFICATION OF REACTIONS.............................. 23

CHAPTER III.

IMPROVEMENT IN THE CONDITIONS OF REACTION. OVERSTRAIN OF REACTIONS.............................. 48

CHAPTER IV.

INFLUENCE OF NEIGHBORING ATOMS AND ATOMIC COMPLEXES.. 76

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APPLICATION OF SOME GENERAL REACTIONS TO INVESTIGATIONS IN ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY. FIXATION OF LABILE HYDROGEN ATOMS.

ALL investigations in the domain of organic chemistry are based, in the firmest and most complete manner, on those parts of general theory which apply to the carbon atom, but only a comparatively small number of them retain these higher and more exhaustive points of view in the experimental portions of the work. Should the desired result not be obtained by one method, another, apparently more or less suitable, is tried, the selection being usually haphazard. The time has arrived when it is possible to formulate, for the conduct of some operations, a number of general rules derived from the enormous mass of experimental material which has accumulated, and, as a corollary, to develop considerably many methods which are in use for organic chemical investigations. It may be hoped that, in course of time, the blind, trial and failure process may be increasingly restricted; this little book is offered as an attempt to systematize methods of work, and treats of the following topics: *fixation of labile hydrogen atoms; modification of reactions; improvement in the conditions of reaction by due recognition of the circumstances in which the product is formed; influence of neighboring atoms and atomic complexes;* also some remarks on the *"overstrain" of reactions.*

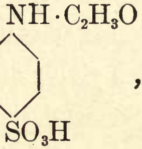
FIXATION OF LABILE HYDROGEN ATOMS.

Before the actual investigation can be commenced it is frequently of the greatest importance to fix, or protect, highly reactive (labile) hydrogen atoms which are present in the material to be used or in the reagents. Methods suitable for this purpose are now frequently employed, but obviously they are only applicable where the investigation is not concerned with the behavior of the labile hydrogen atom in the mother-substance. The object of fixation is to prevent the hydrogen atom participating in reactions, and so either complicating the phenomena or entirely inhibiting the change which it is desired to investigate. Fixation is accomplished by substituting for the hydrogen some suitable atom or group which must be of such a nature that it will easily take the place of the hydrogen atom in the mother-substance, and be itself readily displaced from the product of the main reaction by hydrogen, which must enter the molecule in its original position. Although the term "fixation" is employed to designate this procedure, it will be readily understood that it consists of substitution and reverse substitution. At present fixation is only *universally* employed for the amino hydrogen in the nitration of aromatic amines, but it is just as important and suitable for the protection of the hydrogen of hydroxyl and imino groups if these are present in the compounds under investigation. Even in the case of the amino derivatives nothing of general application is at present known, although, as will be apparent from what follows, a very large number of isolated facts have been recorded. A considerable amount of work in various directions has been done on the preparation of mononitranilines, and a brief consideration of it will best illustrate the present state of knowledge of the subject of this chapter.

Failure must, of necessity, attend any attempt to nitrate directly, by means of nitric acid, compounds containing the amino group, because the acid oxidizes this group more rapidly than it attacks the nucleus.

In these circumstances, at an early stage of the investigation of aniline, attention was directed to the provision of methods of protecting the amino group during the nitration process, or of fixing one or both of the hydrogen atoms. In the case of aniline protection may be obtained by dissolving it, before nitration, in a large proportion of concentrated sulphuric acid; this excess of acid restricts the action of the nitric acid to the nitration of the nucleus, and, as the amino group is protected, the complete decomposition of the molecule is prevented. The chief product of the reaction is metanitraniline, but a mixture of ortho and paranitraniline is obtained by the addition of aniline nitrate to concentrated sulphuric acid.

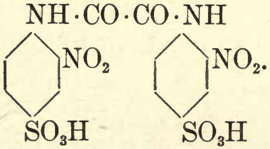
These two methods are, of course, only applicable to such amines as are stable towards sulphuric acid; those about to be described, although hitherto only employed in the case of aniline, appear to be of tolerably general utility. A consideration of acylated anilines shows that the nitration of acetanilide yields a mixture of the three nitranilines, the para derivative predominating. Benzanilide behaves in a similar manner, except that the proportion of meta compound is small. These acylanilides were the first to be employed on a large scale for the preparation of pure orthonitraniline, but their use proved to be so troublesome that since 1885 it has been superseded by the following indirect method. Acetanilide is converted into paracetanilide sulphonic acid,



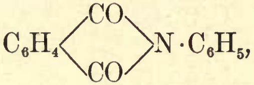
,

which is nitrated in sulphuric acid solution; the nitro group enters in the ortho position relative to the acetamino group because the para position is occupied. The acid solution is diluted and boiled, the dilute sulphuric acid hydrolyzes the acetamino group, and the resulting, readily soluble, nitrosulphanilic acid is precipitated by means of hydrogen chloride. The conversion of the nitrosulphanilic acid into orthonitraniline is effected by heating the former with hydrochloric acid, under pressure, at 170°–180°.

Apart from the indirectness of the method, it suffers from the further disadvantages that chemically pure acetanilide must be employed, and that, during the sulphonation, the temperature must not be allowed to rise unduly; in consequence of these drawbacks it is unsuitable for general use by the inexpert. Since 1889 orthonitraniline has been easily obtainable, in large quantity, by means of a patented process which requires no special precautions, and does not involve the use of sealed tubes. Oxanilide, which is the starting-point in the process, is sulphonated by means of concentrated sulphuric acid; in this case also the sulphonic group occupies the para position. The product of the reaction is cooled to 40°–50°, and treated with nitric acid, which yields dinitroxanilidodisulphonic acid,

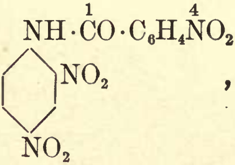


The elimination of the oxalyl and sulphonic radicles from this compound is readily accomplished by adding water and boiling at 120°–150° in a reflux apparatus. At first there is a considerable gas evolution, due to the decomposition of the oxalyl group; later the boiling proceeds quietly, and after several hours the sulphonic radicle is eliminated. The yield of orthonitraniline is 75 per cent. of the crude oxanilide employed. The readiness with which the oxalic acid radicle is eliminated and decomposed by means of dilute sulphuric acid would indicate for it a more extended use than it has hitherto received. In addition to its employment in the preparation of orthonitraniline it has been successfully adapted to the preparation of dinitrodiaminoanthraquinone from diaminoanthraquinone; this is converted into the oxalyl derivative, and the latter nitrated in concentrated sulphuric acid solution. The reactions take place most readily. In 1903 a patent was granted for a process which not only allows of the convenient preparation of paranitraniline, but also permits of the regeneration of original acylated substance. The reactions are as follows: phthalanil,



is nitrated and yields chiefly paranitrophthanil, which, when heated with aniline under pressure, liberates paranitraniline and regenerates phthalanil.

Derivatives of aniline and nitro acids may be used for the production of higher nitrated derivatives; thus paranitrobenzanilide, in concentrated sulphuric acid solution, yields, on treatment with nitric acid, paratrinitrobenzanilide,



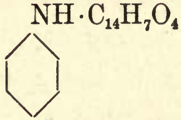
and, by hydrolysis, dinitraniline. This method of preparing dinitraniline is mentioned here, because hitherto it has not been adapted for the preparation of a mononitraniline.

Acyl derivatives of aniline are by no means the only ones which have been employed for the production of nitro derivatives; the readiness with which the amino group combines with aldehydes has led to the use of these compounds also for nitration purposes. A typical derivative of this class is benzylidenaniline,

$$C_6H_5\cdot CH : N\cdot C_6H_5,$$

from benzaldehyde and aniline; it is a somewhat unstable substance, and is readily resolved into its constituents by the action of dilute acids at the ordinary temperature. On account of the absence of water, and therefore of hydrogen and other ions, hydrolysis of the benzylidene derivative does not occur in concentrated sulphuric acid solution, and it is found by experiment that such a solution is readily nitrated without the production of resinous bodies; subsequent dilution of the acid liquid causes separation of the free nitro product. By means of this method aniline yields 90 per cent. of paranitraniline. Solution of the benzylidenaniline in glacial acetic acid, addition of acetic anhydride, and subsequent nitration yields, in addition to paranitraniline, 15 per cent. of the ortho derivative together with resinous products. The experimental conditions here are obviously more complicated than in the previous case.

Purpurin (trihydroxyanthraquinone) has also been employed for the purpose of combining with aniline, which is subsequently nitrated; the purpurin anilide,



in concentrated sulphuric acid solution, is treated with nitric acid, and, by boiling the resulting product with sulphuric acid (70 per cent.), purpurin and orthonitraniline are obtained.

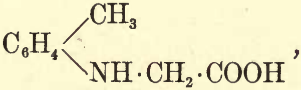
This appears to exhaust the list of readily decomposable aniline derivatives which have been employed for the production of mononitranilines; subsequent reference will be made to the production of ortho, meta, and paranitranilines by the partial reduction of a mixture of ortho and metadinitrobenzene, or by its treatment with ammonia, and also by the action of alcoholic ammonia on ortho and parachloronitrobenzene (*vide* p. 84). These methods have all been tested in the laboratory, but, strictly speaking, they have nothing to do with the nitration of aniline. The same is true of a more recently described process for the production of ortho and paranitraniline, from the corresponding chloronitrobenzenes, by interaction with aqueous ammonia at 170°. The yield is practically quantitative.

A consideration of the previous pages demonstrates that even in the case of aniline, which has been the subject of so many researches, our knowledge is fragmentary, yet it is also practically certain that an exhaustive systematic investigation of the whole field would lead to the discovery of regularities; the position with respect to the amino group taken by the nitro group on its entry into the aniline molecule can scarcely be a matter of chance, but must be subject to definite rule. The influence exercised by the acyl or other aliphatic or aromatic radicle which is introduced into the amino group will also be capable of formulation as soon as systematic investigations have been carried out on the influence of these groups, as such, and of their alkyl, halogen, and other substitution products. The conclusions thus drawn may then be tested in the case of other amines, and ultimately it will be possible to see whether the regularities are universally valid for amines or only for the various classes of them. The investigation would also naturally include the diacylated amines, now that they are readily obtainable, especially as so very little is known of their behavior towards nitrating agents.

Fixation of amino hydrogen by means of alkyl is less interesting than by the use of the acyl and other groups mentioned above; although the preparation of methyl and ethyl derivatives from dimethylic and diethylic sulphates is extremely easy, and these two compounds are now readily available, the subsequent treatment of the alkyl amines offers difficulties because the final elimination of alkyl takes place much less readily than that of acyl, the benzylidene group, etc.

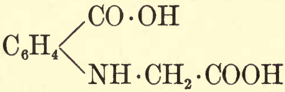
Some other cases may now be considered which illustrate the convenience or necessity of fixing the hydrogen atoms linked to nitrogen in carrying out reactions other than nitration; they will also serve to demonstrate that the influence of fixation extends beyond the amino group primarily concerned.

Mauthner and Suida state that the tolylaminoacetic acid,



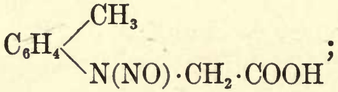
$$C_6H_4\Big\langle\begin{matrix}CH_3\\ NH\cdot CH_2\cdot COOH\end{matrix},$$

from chloracetic acid and toluidine, is not oxidized to the corresponding acid,



$$C_6H_4\Big\langle\begin{matrix}CO\cdot OH\\ NH\cdot CH_2\cdot COOH\end{matrix}$$

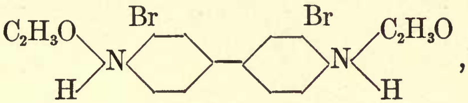
This latter compound, which is now termed phenylglycinecarboxylic acid, subsequently acquired a great interest on account of its connection with the synthesis of indigo. A further investigation of its behavior towards oxidizing agents showed that the methyl group is readily attacked by them if the imide hydrogen is replaced by acyl. During the process of acylation a portion of the tolylaminoacetic acid is lost in consequence of its decomposition with elimination of carbonic anhydride; therefore, in order to avoid this, an entirely different process has been worked out for the fixation of the hydrogen atom. The acid is nitrated by means of sodium nitrite, an operation which is readily carried out and gives an excellent yield of the nitroso derivative,



$$C_6H_4\left\langle\begin{matrix}CH_3\\ N(NO)\cdot CH_2\cdot COOH\end{matrix}\right. ;$$

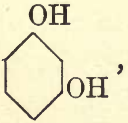
this, with permanganate, gives nitrosophenylglycinecarboxylic acid. The elimination of the nitroso group is readily accomplished by dissolving the acid in sodium carbonate solution, and boiling with zinc-dust and sodium hydroxide until ammonia ceases to be evolved. The phenylglycinecarboxylic acid is then precipitated by means of hydrochloric acid. The course of this remarkable reaction could not have been foreseen, and even after it had been demonstrated it remains a matter for surprise that the original nitroso derivative should not yield either a nitro acid or undergo decomposition.

The oxidizing action of halogens often becomes inconveniently prominent during the process of substitution of compounds containing free amino or hydroxyl groups; aniline, for example, must be converted into acetanilide before it can be quantitatively brominated, and the same is true of α-naphthylamine. Benzidine is so sensitive towards chlorine and bromine that it is scarcely possible to obtain substitution products directly; diacetylbenzidine, however, gives a quantitative yield of the dibromo-derivative,



from which the acetyl groups may be eliminated by boiling with sulphuric acid (50 per cent.).

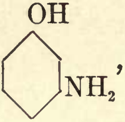
The behavior of a compound during its conversion into a hydroxyl derivative differs according to whether it originally contained hydroxyl or amino groups, but in all cases the greater sensitiveness of the latter radicle is noticeable. Fusion of phthalic anhydride and resorcinol,



yields fluoresceïn,

$$C_{20}H_{10}O_3(OH)_2,$$

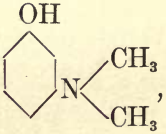
but direct heating of the anhydride with metaminophenol,



does not yield the corresponding rhodamine,

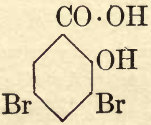
$$C_{20}H_{10}O_3(NH_2)_2;$$

the latter is, however, readily obtained by dissolving metaminophenol hydrochloride in a considerable quantity of concentrated sulphuric acid, adding the anhydride, and heating at 180°–190°. The sulphuric acid here affords the necessary protection to the amino group. In contrast with metaminophenol, metadimethyl aminophenol,



in which the amino hydrogen is fixed beforehand, yields tetramethylrhodamine by direct fusion with phthalic anhydride. In this connection the following observation is of interest; benzaldehyde and paranitrobenzylcyanide readily condense in presence of sodium ethoxide, but the corresponding reaction with orthaminobenzaldehyde does not take place; it can, however, be easily brought about by the use of an acyl derivative; acetyl aminobenzaldehyde was the compound actually employed.

A study of the hydroxyl in carboxyl groups shows conclusively that the replacement of the hydrogen by metal, i.e., the use of a salt instead of the free acid, not only facilitates a reaction, but is frequently the factor which determines whether it shall or shall not take place. The employment of solutions of salts, instead of the free acids, is advantageous in such operations as the treatment of acids with alkaline reagents. In dealing with aromatic hydroxy acids it is best to dissolve them in a considerable excess of potassium hydroxide solution, which causes the phenolic hydrogen to be replaced by metal. The interaction of salicylic acid and potassium hypochlorite proceeds most easily if the acid is previously dissolved in aqueous potassium hydroxide (2 mol.). A further example, which has just been worked out by the author, is afforded by the action of dipotassium salicylate on the calculated quantity of recently prepared potassium hypobromite, in aqueous alkaline solution, at 0°. After remaining for a short time the solution is acidified and a copious precipitate of dibromosalicylic acid,



is obtained. The purification of the acid is most conveniently accomplished by the preparation and subsequent decomposition of its ammonium salt, which is very sparingly soluble at the ordinary temperature; recrystallization of the crude acid from water is not a convenient method for removing impurities. The purified acid is very sparingly soluble in boiling water, melts at 222°, contains 54.05 per cent. of bromine, and, on treatment with methylic alcohol and sulphuric acid, yields a methylic salt which melts at 150°. These facts establish the composition of the acid and show it to be identical with one prepared by Lellmann and Grothmann[1] by the action of bromine (5 atoms), on salicylic acid in dilute glacial acetic acid solution. A similar iodo acid has been prepared by the same method: the iodine was determined by the convenient wet process recently described by Baubigny and Chavanne.[2] The use of salicylic acid in alkaline solution, as above described, obviously results in the saving of a considerable quantity of bromine.

The conclusions drawn from the foregoing facts are undoubtedly applicable to amino hydrogen; it is well known that the conversion of phthalimide into anthranilic acid by means of sodium hypochlorite, à reaction which is now of such great importance in the synthesis

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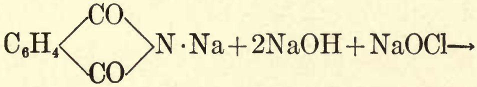
Berichte d. deut. Chem. Gesell. **17**, 2728.

[2] Compt. rend. 1903, **136**, 1198.

of indigo, only yields good results if alkali is present in quantity sufficient to convert the imide into its sodium salt, in accordance with the equation



$$C_6H_4\langle{}^{CO}_{CO}\rangle N\cdot Na + 2NaOH + NaOCl \rightarrow$$
$$NH_2\cdot C_6H_4\cdot COONa + Na_2CO_3 + NaCl.$$

It will now be convenient to consider the case of a reaction which it is desired to employ the progress of which would be hindered, or completely inhibited, by the free hydroxyl of the carboxyl group. The behavior of aminoacetic acid towards nitrous acid affords one of the best examples in this connection. Very numerous attempts have undoubtedly been made to convert aminoacetic acid hydrochloride into diazoacetic acid, but always without success. In 1884 an entirely new field of research was opened up by the discovery that ethylic aminoacetate hydrochloride could be easily converted into ethylic diazoacetate; in other words, the desired reaction readily takes place if the hydrogen of the carboxyl group is fixed (replaced) by ethyl. Oxalyl chloride was unknown until 1892, because it cannot be prepared directly from oxalic acid and phosphorus pentachloride; it is, however, readily obtained from ethylic oxalate and phosphorus pentachloride. Sodium derivatives of acetoacetic acid, malonic acid, and similar compounds, in which the methylene hydrogen is replaced, cannot be prepared from the free acids, but are readily obtained from the ethereal salts, and are widely used on account of their great reactivity. No definite products can be formed by the interaction of phosphorus pentabromide and malic acid, either directly or in chloroform solution, but the use of malic esters leads to the production of bromosuccinic esters. Similar results are observed in the case of tartaric acid; by the action of phosphorus tribromide, in chloroform solution, at low temperatures, on the ethylic salt, ethylic bromomalate,

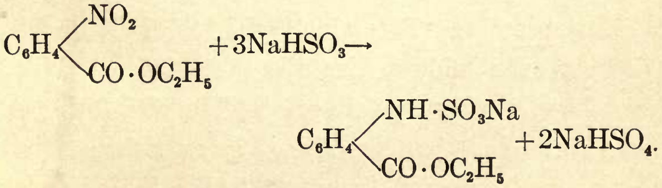
$$C_2H_5O \cdot CO \cdot CH \cdot OH \cdot CHBr \cdot CO \cdot OC_2H_5,$$

is obtained.

In many other cases, greatly differing from the foregoing, the use of ethereal salts instead of free acid has been proved to be very advantageous even if not absolutely necessary. It is very probable that ethylic sulphanilate would be more readily reduced by means of sodium and amylic alcohol than the free acid; it has been shown, by direct experiment, that this is the case with ethylic methyldihydroxybenzoate in spite of the fact that, during the reduction, a portion of the ethylic salt is hydrolyzed by the sodium amyloxide.

The yield of position isomers obtained by the nitration, sulphonation, etc., of aromatic acids differs widely according to whether the reaction is carried out by means of the free acid or the ethereal salt. The nitration of cinnamic acid results in the almost exclusive production of the para compound together with a very little of the ortho derivative; ethylic cinnamate, under similar conditions, yields 70 per cent. of ethylic orthonitrocinnamate.

The behavior of aromatic nitro acids and their ethereal salts towards sodium bisulphite also differs greatly. It is well known that, by this method of reduction, not only is the nitro group converted into the amino radicle, but simultaneously one or more sulphonic radicles may enter the nucleus, so that it is possible to pass directly from a none sulphonated nitro acid to a sulphonic amino compound. Treatment of the ethereal salts of nitro acids with sodium bisulphite results in the reduction of the nitro group, and the replacement by the sulphonic radicle of one hydrogen atom in the resulting amino group, but the nucleus is not attacked. A new and convenient method is thus supplied for the preparation of sulphaminic acids:



$$C_6H_4\left\langle\begin{matrix}NO_2\\ CO\cdot OC_2H_5\end{matrix}\right. + 3NaHSO_3 \rightarrow C_6H_4\left\langle\begin{matrix}NH\cdot SO_3Na\\ CO\cdot OC_2H_5\end{matrix}\right. + 2NaHSO_4.$$

The methyl and ethyl radicles are not the only ones employed for the fixation of hydrogen in carboxyl; it is often extremely advantageous for the conduct of the reaction to substitute the hydroxyl by means of chlorine or bromine; this method has the further merit of permitting the restoration of the hydroxyl to take place with extreme ease. The readiness with which acid bromides may be brominated is illustrated by Dolhard's admirable method for the preparation of monobrom acids in open vessels. Dibromohexahydrophthalic acid is obtained by treating the mother-substance with phosphorus pentachloride in an open tube, to the resulting acid chloride the calculated quantity of bromine is added, the tube sealed, and heated at 150°. Camphoronic acid does not yield a substitution product by treatment with bromine alone or when mixed with phosphorus tribromide, but a brom acid is readily obtained by heating camphoronic chloride with bromine.

The method of fixation of hydrogen, referred to in connection with hydroxy acids, is also applicable to phenolic derivatives. Pyrocatechol and hydroquinone are oxidized, but not brominated, by the action of nascent bromine. Resorcinol, the third isomeride, yields a tribromide under these conditions. When several hydroxyl groups are present in a ring their protection (fixation) is often almost as essential as that of the amino group; hydroquinol, for example, can only be conveniently nitrated in the form of its diacetyl derivative,

$$C_6H_4(\overset{1,4}{OC_2}H_3O)_2.$$

Gallic acid,

$$C_6H_2(OH)_3 \cdot COOH,$$

is oxidized to oxalic acid by means of nitric acid, but triethoxygallic acid,

$$C_6H_2(OC_2H_5)_3 \cdot COOH,$$

is nitrated with tolerable readiness, and yields, by loss of carbonic anhydride, nitrotriethoxypyrogallol. It is probable that the nitration of ethylic triethoxygallate,

$$C_6H_2(OC_2H_5)_3 \cdot CO \cdot OC_2H_5,$$

would proceed without loss of carbonic anhydride, but the experiment does not appear to have been tried. In conclusion, it may be pointed out that bromonitromethane cannot be obtained directly from nitromethane; if, however, the latter is converted into sodium nitromethane,

$$CH_2 \cdot NO_2 \cdot Na,$$

so as to fix the labile hydrogen atom, the desired compound is produced by the action of bromine,

$$O_2N \cdot CH_2 \cdot Na + Br_2 \rightarrow O_2N \cdot CH_2 \cdot Br + NaBr.$$

The contents of this chapter demonstrate clearly that the fixation of labile hydrogen atoms is a necessity or convenience in compounds of widely differing constitution which are to be made the starting-points of research. Other examples to the same effect will be encountered later.

CHAPTER II.

MODIFICATION OF REACTIONS.

THE modification of reactions is accomplished by suitably modifying or varying the reagents employed. It may be convenient to open the subject by a consideration of the relative advantages accruing from the use of sodium or potassium derivatives. It is undoubtedly true that, in many cases, and in reactions of widely differing nature, practically identical results are obtained by the use of compounds of either metal. This rule is, however, by no means of universal applicability; indeed experiment often shows that the exact opposite is true, and if a reaction has given good results with a potassium compound, it is always necessary to ascertain, by direct trial, what effect will be produced by the use of the sodium derivative, assuming, of course, that the question is of sufficient interest to justify the work.

Metallic potassium is assuredly far more reactive than metallic sodium: the former reacts violently with anhydrous bromine, the latter does not. It may be

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confidently expected that the present relatively high price of potassium will soon be reduced, so that one drawback to its use will be overcome. Potassium has recently been prepared by heating aluminium with potassium fluoride or potassium silicofluoride in a retort. As no carbon monoxide is produced by this process, it constitutes the first distillation method, free from danger, which has been devised for the preparation of potassium. Pure potassium will probably prove to be too violent in its action, but it may be modified by the use of the liquid potassium-sodium alloy, which can be regarded as being diluted potassium. Its employment is extremely convenient, because it usually floats, in the form of globules, on the substances which are present; in all cases of its use the potassium reacts in preference to the sodium.

Potassium amalgam will doubtless also often supersede sodium amalgam. In cases where the action of both these substances is too energetic it is often convenient to employ aluminium amalgam, which possesses the further advantage of producing hydrogen in *neutral* liquids:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3H.$$

Magnesium amalgam is also extremely useful and has a similar application.

The following examples illustrate the superior reactivity of potassium compounds over those of sodium: Ethylic sodiomalonate and ethylic dimethylacrylate yield, in an open vessel, only 8 per cent. of the theoretical quantity of ethylic tricarboxylate; the use of ethylic potassiomalonate increases the yield to 35 per cent. The maximum yield of phenylacetic acid is 14 per cent., if it is prepared by heating a mixture of phthalic anhydride, acetic anhydride, and sodium acetate; the substitution of potassium acetate not only accelerates the reaction, but increases the yield to 50 per cent. Potassium tartrate, phenol, and phosphorus oxychloride yield diphenylic tartrate, but this compound is not produced from sodium tartrate. The interaction of chloracetone and sodium paranitrophenolate is accompanied by considerable decomposition, but the substitution of the potassium salt results in a yield of 50 per cent. of paranitrophenacetol.

The regulation of a reaction may also be accomplished by the use of ammonium salts instead of those of the alkali, or alkaline-earth metals. The first preparation of phenylhydroxylamine was made in 1893 by boiling nitrobenzene with water and zinc-dust, and it was shown that only certain samples of zinc-dust are capable of bringing about the reduction. It was then proved that the reaction was favored by the presence of neutral salts, especially of calcium chloride or sodium chloride, but, by this method of working, it is impossible to prevent the formation of azoxybenzene and other compounds intermediate between nitrobenzene and aniline, and, in order to ascertain the progress of the reaction, it is necessary to test successive portions of the product with Fehling's solution and stop the experiment when the maximum reduction is observed. Further work led to the use of the zinc-copper couple, containing only a small proportion of copper, in place of zinc-dust. This was boiled for several hours on the water-bath with nitrobenzene, in ethereal solution, and aqueous calcium chloride, and yielded hydroxylamine derivatives free from by-products. In 1899 it was discovered that the reaction proceeds quantitatively and directly by heating zinc-dust with nitrobenzene and dilute aqueous ammonium chloride solution. In this reaction the ammonium salt is the specific agent, and only in its presence does the change proceed smoothly. The advantages derived from the addition of neutral salts of the alkali, and alkaline-earth metals was quickly discovered, but, in order to obtain a quantitative yield and prevent secondary reactions, it was necessary to modify the action of these reagents, and this is done by substituting an ammonium salt for that of the fixed alkali.

In order to grasp the relative influence on reactions of sodium hydroxide and potassium hydroxide experimental information on the following points must be forthcoming: (I) The result of using aqueous potassium hydroxide in reactions heretofore carried out with the sodium derivative. (II) The substitution of the solvent water by alcohol. (III) The effect of fixing the labile hydrogen atoms in the solvent and reagent by replacing them with methyl or ethyl. In this connection it would be interesting to determine the effect of using the methoxides and ethoxides of the alkaline-earth metals. (IV) In many cases it would be extremely important to ascertain the result of replacing sodium or potassium hydroxide by ammonium, barium, and other hydroxides. These various factors will now be considered in order as far as the available material permits.

(I) The examples given above (p. 23 et seq.) of the differences in behavior of potassium and sodium salts render it unnecessary to adduce further instances of the relatively greater reactivity of potassium hydroxide as compared with sodium hydroxide.

(II) The effect of using an alcohol instead of water as solvent is illustrated by the following examples. In 1877 Zagumenny obtained benzhydrol by the interaction of benzophenone, zinc, and alcoholic potassium hydroxide,

$$(C_6H_5)_2CO + 2H \rightarrow (C_6H_5)_2CH \cdot OH,$$

but the method only became generally applicable in 1884, when amylic alcohol was substituted for the ethylic alcohol. Under these conditions it was possible to convert tetramethyldiaminobenzophenone into its hydrol derivative, which could not be done in ethylic alcoholic solution.

(III) The advantages accruing from the fixation of the hydrogen atom of the hydroxide may now be considered. At present scarcely anything is known of the behavior of potassium ethoxide as a reagent, but it is to be hoped that this state of matters may soon be changed, as it cannot be doubted that its use would frequently be attended by advantageous results. The modification of reactions produced by the substitution of aqueous sodium hydroxide solution by alcoholic sodium ethoxide has been demonstrated in numerous instances. The latter is often superior to the former for the preparation of salts. Bromacetic acid, in ethereal solution, when mixed with the calculated quantity of sodium ethoxide, in alcoholic-ethereal solution, gives a 95 per cent. yield of crystalline sodium bromacetate. The preparation of solid sodium phenoxides is most readily accomplished by adding the calculated quantity of sodium ethoxide to the phenol, in alcoholic solution, and drying the mixture in a current of hydrogen.

As a condensing agent the great superiority, over sodium hydroxide, of sodium methoxide and sodium ethoxide, in the solid state or in solution, is so generally admitted and has been demonstrated in so many instances that it is unnecessary to adduce special examples.

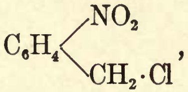
Hydroxylamine hydrochloride had been known for thirty years before the free base was isolated by the use of solid sodium methoxide; subsequently it was obtained by the action of anhydrous barium hydroxide, but all previous attempts to prepare it by the decomposition of its salts by means of solid sodium hydroxide or potassium hydroxide were fruitless. In this connection attention may be directed to the use of the sodium and potassium oxides, M_2O. Until recently these were not known with certainty; now they have been made readily accessible by several methods of preparation, amongst which may be mentioned fusion of a mixture of potassium and potassium nitrite,

$$KNO_2 + 3K \rightarrow 2K_2O + N,$$

where the atmosphere of nitrogen necessary for the conduct of the reaction is furnished by the substance itself; and fusion of sodium peroxide or potassium peroxide with the calculated quantity of the respective metal.

For purposes of hydrolysis sodium ethoxide offers many advantages over sodium hydroxide; the resolution of fats, for instance, by means of sodium ethoxide, takes place in the easiest possible manner, and although their decomposition with alcoholic alkali is not very difficult, the use of aqueous hydroxide for this purpose is decidedly unpleasant to carry out in a laboratory. Some hydrolyses can only be effected by means of sodium ethoxide; so, for instance, in the case of benzoyl *d*-glucose, by the action of sodium ethoxide the benzoyl groups are eliminated and *d*-glucose (dextrose, grape-sugar) regenerated, whereas the use of any other hydrolytic agent results in the *d*-glucose itself being affected. It will undoubtedly be found that in many other instances sodium ethoxide will be the most suitable agent for the elimination of acyl groups from compounds which are thereby rendered unstable, and it will certainly be possible to modify the reaction by the substitution of sodium methoxide or sodium amyloxide. A further means of modification is offered by the use of the alkyloxides of the alkaline-earth metals, instead of those of the alkali metals, and it appears desirable to test this suggestion by experiments with magnesium methoxide, which is now readily available.

In the case of unstable compounds, which are not conveniently hydrolyzed by either alkalies or acids, a further means of modifying the reaction is afforded in the moderation of the alkali or alkaline earth by its combination with a feeble acid such as carbonic acid, or, in other words, by substituting for the hydroxide the salt of a feeble acid. Aliphatic chlorine can frequently be removed by boiling the compound with water and calcium carbonate or sodium carbonate. Orthonitrobenzyl chloride,



$$C_6H_4\left\langle\begin{matrix}NO_2\\CH_2\cdot Cl\end{matrix}\right.,$$

which has been thoroughly investigated in this respect, furnishes a good illustration; it is hydrolyzed by boiling with calcium carbonate and water, but the reaction only proceeds quantitatively by heating it with aqueous sodium carbonate at 85°, i.e., at a temperature below the boiling-point. It is obvious that, in the case of such a sensitive substance, not only the reagent but also the temperature requires modification and control.

When dealing with compounds containing an acyl linked to nitrogen and another combined with oxygen, it is particularly difficult to so control and modify the hydrolytic agent as to remove only one acyl. An example of the successful solution of this problem is afforded by the conversion of diacetylindoxyl,

$$C_2H_3O\cdot O\cdot C_8H_5\cdot N\cdot C_2H_3O,$$

into the monacetyl derivative,

$$HO\cdot C_8H_5\cdot N\cdot C_2H_3O,$$

which cannot be prepared directly. It is obvious that the only reagents suitable for the purpose would be considerably moderated ones, and experiment shows that the result is attained by the use of aqueous solution of sodium sulphite, sodium hydrogen sulphite, or sodium phosphate, but not by that of sodium carbonate.

Especial attention may now be directed to the subject of fusion with alkali. It has long been known that, for this purpose, potassium hydroxide is far superior to sodium hydroxide; for instance, potassium benzenesulphonate, by fusion with potassium hydroxide, yields 96 per cent. of phenol; with sodium hydroxide not more than 25 per cent. can be obtained. It must, however, be recognized that intramolecular rearrangement occurs more readily during fusion with potassium hydroxide than with sodium hydroxide: sometimes this is an advantage, at others it is not; a practical instance of rearrangement is furnished by Kolbe's well-known synthesis of salicylic acid. Until recently the only means employed for modifying this reaction were changes in the temperature and differences in the amount of water employed; in consequence, however, of work on the conversion of phenylglycinecarboxylic acid into indigo various other means of modification have been discovered. Phenylglycinecarboxylic acid has been previously referred to and will be mentioned again later. It was at first converted by fusion with potassium hydroxide, but the yield was extremely poor; better results were obtained by adding quicklime to the potassium hydroxide; subsequently the latter was omitted altogether, and it was found that improvement was effected by fusion of potassium phenylglycinecarboxylate with barium oxide at about 290°. Nothing is reported of the use of sodium hydroxide, but it is practically certain that it would be much less suitable than potassium hydroxide; the use of sodium oxide, which is now readily available, is, however, advantageous, a mixture of this with the potassium salt being employed. The best results of all appear to be given by the addition of sodium ethoxide to the potash fusion. The yield of indigo is 8.6 per cent. of the theoretical with a mixture of sodium and potassium hydroxides; this is increased to 18 per cent. when the hydrogen atom of the sodium hydroxide is replaced by ethyl. In the alizarin fusion it was found that the results were greatly improved if the reducing action of the reagent were inhibited by the addition of an oxidizing agent, such as potassium chlorate. Experiments in this direction have been made with phenylglycinecarboxylate, and they indicate that, although potassium chlorate is not suitable for the purpose, sodium peroxide gives good results.

A general survey of the work on the conversion of phenylglycinecarboxylic acid into indigo, which has been roughly summarized above, shows that here, as in the nitration of aniline, the efforts to improve the yield were not directed from a systematic, wide, generalized point of view, but rather in the hope that, in some haphazard, accidental fashion, a better process might be found. The above results may, however, be regarded as the beginning of an attempt to attain a better yield by the modification of the original reaction involved in the potash fusion; the solution of the problem then ceases to be a case of lucky accident, and becomes only a question of sufficient systematic work carried out along lines already laid down and which must eventually lead to the desired end. There can be no reasonable doubt that the yield of indigo is capable of much improvement, and that this result will be attained by work directed and carried out in the spirit indicated.

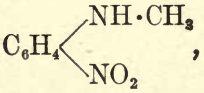
The advantages accruing from the replacement of hydrogen by alkyl are even more marked in the case of ammonia than in that of sodium or potassium hydroxides. Derivatives of ammonia, i.e., organic bases, of all classes, are capable of yielding crystalline salts from mixtures of acids, or of precipitating bases in a crystalline form in circumstances where this cannot be accomplished by the use of any inorganic base. In cases of difficulty the use of brucine salts is often advisable, but frequently the desired result is obtained by means of diethylamine, a much closer analogue of ammonia. An example is furnished by the history of glucosamine; it was first prepared in 1876, in the form of hydrochloride, by boiling crab-shells with hydrochloric acid, and was speedily recognized as being an amino sugar, but all attempts to obtain it in the free state, by means of inorganic bases, were fruitless. After almost thirty years, in 1894, it was found that diethylamine readily liberated it in crystals from the hydrochloride. In this connection diethylamine may be regarded as modified ammonia. As a condensing agent diethylamine is much superior to ammonia, precisely as sodium ethoxide is to sodium hydroxide.

It has long been known that alkalies produce resinous substances from aldehydes and ketones, but by the use of "modified" ammonia derivatives, such as

Hydroxylamine,	$NH_2 \cdot OH$;
Phenylhydrazine,	$NH_2 \cdot NH \cdot C_6H_5$;
Semicarbazine,	$NH_2 \cdot CO \cdot NH \cdot NH_2$;
Aminoguanidine,	$NH_2 \cdot C(NH) \cdot NH \cdot NH_2$;

and similar substances, aldehydes and ketones of the most complicated kind readily yield compounds which crystallize with ease; indeed it is only by the preparation and use of such compounds that certain classes of complex aldehydes and ketones, such as the sugars, could be investigated.

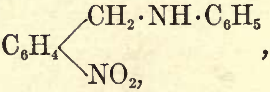
The superiority in reactivity of methylamine to ammonia is illustrated by the partial reduction of orthodinitrobenzene. Its conversion into orthonitraniline proceeds very slowly by the action of alcoholic ammonia in a sealed tube, but it is converted quantitatively into orthonitromethylaniline,



$$C_6H_4\left<\begin{matrix}NH\cdot CH_3\\ NO_2\end{matrix}\right.,$$

by heating it for a few minutes at 100° with methylamine in alcoholic solution. Metadinitrobenzene does not react in this manner, so that the method is the most convenient known for the preparation of orthonitromethylaniline from the mixture of ortho and metadinitro derivatives obtained by the direct nitration of benzene.

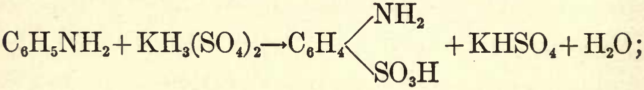
Nitrobenzyl bases, such as orthonitrobenzylaniline,



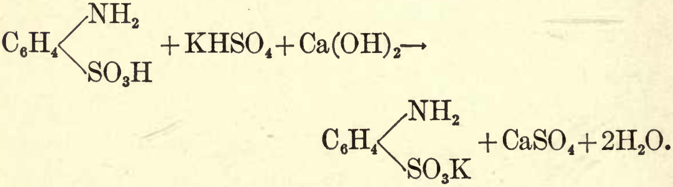
$$C_6H_4\left<\begin{matrix}CH_2\cdot NH\cdot C_6H_5\\ NO_2,\end{matrix}\right.,$$

are not reduced in either acid or ammoniacal solution; in the former decomposition takes place and resinous matter is formed; in the latter the substances obtained are not reduction products. In 1889 it was found that the "modification" of ammonia into aniline readily yields the desired result, the nitro compound, in aniline solution, being easily reduced to aminobenzylaniline.

Modification of the action of acids may be accomplished by many means. The concentrated or fuming sulphuric acid, which is so largely employed for sulphonation, has several drawbacks, perhaps the chief one being its decomposing action on the material to be sulphonated, whereby the yield is diminished and the product contaminated. The fixation of a hydrogen atom by an alkali metal, i.e., the use of a bisulphate instead of the free acid, is not satisfactory, as the conditions under which organic compounds are sulphonated by means of bisulphate are difficult to realize. The results are, however, entirely different if polysulphates are employed instead of bisulphates; potassium trihydrogen disulphate is the most convenient one to use, as it melts at the temperature of a boiling water-bath and can, consequently, be employed under the same experimental conditions as sulphuric acid itself. Moreover, the introduction of more than one sulphonic group can be accomplished by the use of higher temperatures. A further advantage offered by this potassium compound is that, after the sulphonation, the molecular ratio of sulphonic acid to potassium hydrogen sulphate is such that it is only necessary to neutralize the free acid by means of milk of lime in order to obtain directly the potassium salt of the sulphonic acid, as is shown by the following equations for the sulphonation of aniline:



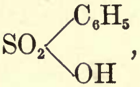
$$C_6H_5NH_2+KH_3(SO_4)_2\rightarrow C_6H_4{<}\begin{matrix}NH_2\\SO_3H\end{matrix}+KHSO_4+H_2O;$$



$$C_6H_4{<}\begin{matrix}NH_2\\SO_3H\end{matrix}+KHSO_4+Ca(OH)_2\rightarrow$$
$$C_6H_4{<}\begin{matrix}NH_2\\SO_3K\end{matrix}+CaSO_4+2H_2O.$$

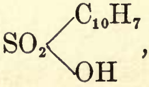
Phenylsulphonic acid is obtained far more readily from potassium trihydrogen disulphate than from sulphuric acid. With the latter the yield is not particularly good, even if a large excess of acid is employed, unless the mixture is absorbed by ignited infusorial earth and allowed to remain for some time; under these circumstances the yield is quantitative (*vide* p. 82).

Admirable agents for etherification and esterification are furnished by phenylsulphonic acid,



$$SO_2{<}\begin{matrix}C_6H_5\\OH\end{matrix},$$

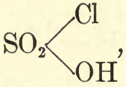
and naphthylsulphonic acid,



$$SO_2{<}\begin{matrix}C_{10}H_7\\OH\end{matrix},$$

which may be regarded as sulphuric acid "modified" by the replacement of one hydroxyl by means of phenyl or naphthyl; Krafft and Roos state that, for the manufacture of ether from alcohol, phenylsulphonic acid is superior to sulphuric acid.

Modification of sulphuric acid, in the sense of increasing its activity, is effected by the replacement of a hydroxyl by means of chlorine; the resulting sulphuryl chloride,



$$SO_2 \begin{cases} Cl \\ OH \end{cases},$$

may be used for the sulphonation of substances which are only little, if at all, affected by ordinary or fuming sulphuric acid, and also in cases where the latter reacts too energetically.

It is well known that, in addition to its sulphonating action, sulphuric acid readily causes both intramolecular and extramolecular dehydration. Such reactions and condensations often proceed smoothly; but frequently, in order to obtain good results, it is necessary to modify the acid so as to reduce its decomposing power. Until 1895 amylene was always prepared by dehydrating amylene hydrate by means of sulphuric acid.

$$(CH_3)_2\cdot COH\cdot CH_2\cdot CH_3 \rightarrow (CH_3)_2\cdot C : CH\cdot CH_3 + H_2O.$$

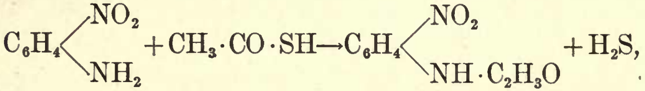
Irrespective of whether concentrated or dilute acid was employed, the amylene was always contaminated by condensation compounds of high boiling-point. The results were not improved by the use of zinc chloride, or phosphoric anhydride in place of sulphuric acid, but by adding the tertiary alcohol, in a continuous stream, to oxalic acid at 90°, water and amylene distil over together, the decomposition proceeds regularly for an indefinite time, and all secondary actions are avoided.

The use of an organic acid in place of an inorganic one is a method of modifying a reaction which is capable of wide application, as is shown by the following examples, in addition to the one just given. Paranitroacetanilide is not reduced by means of tin and hydrochloric acid, because of the hydrolytic action of the acid, but iron and acetic acid readily convert it into aminoacetanilide. The use of hydrochloric acid for reduction purposes frequently leads to the introduction of chlorine into the reduced compound. As a rule the proportion of chloro derivative formed is small, but it is the chief product of the interaction of orthonitrobenzylsulphonic acid, tin, and hydrochloric acid, the yield of chloraminobenzylsulphonic acid being 70 per cent., together with a certain amount of the aminosulphonic acid; the nitro compound is, however readily reduced by means of iron and acetic acid in place of tin and hydrochloric acid, an excellent yield of aminobenzylsulphonic acid being obtained.

The use of halogen acids, under appropriate conditions, may also be regarded as a method of modifying reactions. Hydrogen bromide dissolves more readily in water than hydrogen chloride, and its equivalent solutions have higher boiling-points; in consequence of this, orthodinitrodibenzylcyanide is readily hydrolyzed to orthodinitrodibenzylcarboxylic acid by heating it in an open vessel with highly concentrated hydrobromic acid, but the reaction does not take place with hydrochloric acid. Similar results have been obtained with other cyanides, and also with certain esters.

In this connection it may be mentioned that recent observations show that silicotungstic acid is much superior to phosphotungstic acid or molybdotungstic acid for the separation of alkaloids. The precipitates given by the last two are frequently amorphous and of varying composition, whereas those obtained by the first are stable, well defined, and frequently crystalline, and, on account of their constancy of composition, are suitable for direct analysis.

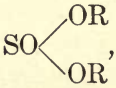
The modification of the oxygen of acids by means of sulphur, i.e., the use of thio-acids in place of carboxylic acids, may now be considered. The only acid studied at all closely in this sense is acetic, and excellent results have been obtained. Acetic acid alone can only be employed for acetylation purposes in exceptional cases, but thiacetic acid is very generally applicable, and the yields are good. It interacts directly with nitraniline for example, in accordance with the equation



$$C_6H_4\begin{cases}NO_2\\NH_2\end{cases} + CH_3\cdot CO\cdot SH \rightarrow C_6H_4\begin{cases}NO_2\\NH\cdot C_2H_3O\end{cases} + H_2S,$$

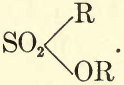
the yield of nitracetanilide being 95 per cent. If it should be found possible to carry out the reaction in the presence of substances capable of absorbing the hydrogen sulphide which is produced, in the same manner that dehydrating agents are employed to absorb the water formed by acetylation with acetic acid itself, it is certain, as will be shown later, that the use of thiacetic acid will be found to be capable of very wide extension, and that the results obtained from it will be considerably improved.

In the preceding pages the only salts which have been mentioned have been those of the alkali metals; it will now be convenient to extend the subject and consider the use of those of other metals. It is well known that salts vary greatly in reactivity; indeed different salts of the same acid do not always yield corresponding decomposition products. Alkyl sulphites,



$$SO\begin{cases}OR\\OR\end{cases},$$

are obtained from sodium sulphite and alkylhaloïds; silver sulphite, under the same conditions, yields sulphonic esters,



$$SO_2 \begin{array}{l} \diagup R \\ \diagdown OR \end{array} .$$

Potassium cyanide and alkyl haloïds produce cyanides, RCN, but with silver cyanide isomeric carbylamines, RNC, are obtained. Silver xanthate and methyl iodide give a methylxanthine which is not identical with theobromine, but this compound is formed if the amorphous silver salt is replaced by the crystalline lead derivative.

The extensive use of aluminium chloride for synthetical purposes does not entirely inhibit the necessity for occasionally modifying it by the substitution of sublimed ferric chloride; this acts less energetically, and for many ketonic syntheses is preferable to aluminium chloride. The action of the two chlorides is analogous in all respects, and similar intermediate products are formed; for example, benzoyl chloride in carbon bisulphide solution, yields the crystalline additive compound

$$C_6H_5COCl \cdot FeCl_3.$$

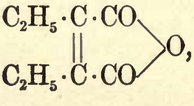
In certain cases the use of inorganic salts may be entirely avoided by employing, in their place, esters of the acid; thus sodium nitrite may frequently be substituted by amylic nitrite for diazotizing. Amongst other advantages which the latter affords is the opportunity of working in solvents other than water; the majority of diazonium salts are very readily soluble in water, so that their preparation in the solid form depends on its exclusion and therefore on the use of amylic nitrite.

Ethylic nitrate is an admirable nitrating agent, and can be advantageously used in place of nitric acid in the case of compounds, such as amides, which do not form nitrates, or only yield them with difficulty; for instance, urethane,

$$NH_2\cdot CO\cdot OC_2H_5,$$

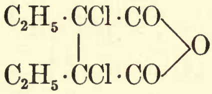
can be readily nitrated in sulphuric acid solution by means of ethylic nitrate.

This section may be concluded by a consideration of reactions involving the necessity for the modification of the halogens and the derivatives of them which are used as reagents, in so far as this modification concerns the halogen atoms which they contain. Chlorine is the most generally reactive halogen; the double linkage in xeronic anhydride,



$$\left.\begin{array}{l} C_2H_5\cdot C\cdot CO \\ \qquad\ \, \| \\ C_2H_5\cdot C\cdot CO \end{array}\right> O,$$

is not affected by bromine, but is very readily resolved by means of chlorine, the compound



being formed. Silver salts behave very differently with different haloïds; silver phthalate is not affected by benzylchloride or paranitrobenzylchloride, but readily reacts with the corresponding iodine derivatives. Paranitrobenzyl phthalate may of course be obtained by a different method, viz., by the action of phthaeylchloride on paranitrobenzyl alcohol, in which the calculated quantity of sodium has been dissolved.

Ethylene chloride and ethylic sodiomalonate yield ethylic butanetetracarboxylate,

$$(C_2H_5O \cdot CO)_2CH \cdot CH_2 \cdot CH_2 \cdot CH(CO \cdot OC_2H_5)_2;$$

the yield is much less with ethylene bromide, and the use of ethylene iodide results in the production of ethylic acetylenetetracarboxylate,

$$(C_2H_5O \cdot CO)_2CH \cdot CH \cdot (CO \cdot OC_2H_5)_2,$$

and evolution of ethylene. Ethylic chloride, in boiling alcoholic solution, is without action on silver nitrate, but ethylic bromide under these conditions yields ethylic nitrate. Phenylhydrazine and ethylic iodide interact with explosive violence, but with ethylic bromide the reaction proceeds quietly, and may be completed by boiling the substances in a reflux apparatus during several hours. The propylic derivative of benzylcyanide is easily obtained by the action of propylic iodide, but not from propylic bromide. By means of ethylic bromacetate or ethylic iodacetate the group

$$CH_2 \cdot CO \cdot OC_2H_5$$

may be readily introduced into desoxybenzoïn, but ethylic chloracetate is not suitable for this purpose. In many cases halogens may be removed from pyridine derivatives by means of sulphuric acid and iron filings; the method is successful in the case of iodolepidine, but fails in the case of the chloro-derivative.

The employment for alkylation purposes of dimethylic sulphate or diethylic sulphate, instead of methylic iodide or ethylic iodide, avoids the necessity for the use of sealed tubes; the two sulphates are now readily accessible, and consequently, for both reasons, the method affords a welcome means of modifying one acid, hydriodic, by the substitution of another, sulphuric.

Since the preparation of fluorine compounds has ceased to offer special difficulties, the question must be raised as to their reactivity and the extent to which they may be advantageously employed for modification purposes.

CHAPTER III.

IMPROVEMENT IN THE CONDITIONS OF REACTION.

It has been recognized for a long time that nitration by means of a nitro acid effects an improvement in the conditions of the reaction. The use of the method implies that due consideration has been given to the circumstances prevailing during the formation of the product. The nitration of benzene proceeds practically quantitatively because the concentrated sulphuric acid which is present absorbs the water produced during the reaction, and so prevents dilution of the nitric acid.

The formation of hydrogen chloride, as a by-product, is of very common occurrence; for instance, in acylation by means of acid chlorides. This method of acylation only achieved its present wide application after the discovery that the reaction proceeded readily, at the ordinary temperature, if the hydrochloric acid were absorbed while in the nascent state. At first this result was produced by allowing the substances to interact in presence of aqueous sodium hydroxide solution; in this form the method was available for many substances, but failed in some cases; fixation of the hydrogen atom of the sodium hydroxide by means of ethyl or some similar group, i.e., the use of sodium ethoxide, in place of sodium hydroxide, for the absorption of the acid greatly increased the sphere of usefulness of the process. This modification has proved of special value in cases where the substance to be acylated is unstable towards sodium hydroxide. It sometimes happens that it is necessary to entirely avoid the use of caustic alkali; in these circumstances potassium carbonate is frequently found to give excellent yields of the desired compound, provided the proportions employed are such as to result in the formation of bicarbonate, as shown by the equation

$$XH + Cl \cdot CO \cdot R + K_2CO_3 \rightarrow X \cdot CO \cdot R + KCl + KHCO_3.$$

Potassium carbonate is, however, unsuited for use in the preparation of certain diphenolic derivatives, on account of their extreme sensitiveness towards hydrolytic agents. The compound formed from pyrocatechol and ethylic chlorocarbonate,

$$C_2H_4(OH)_2 + 2Cl \cdot CO \cdot OC_2H_5 \rightarrow C_6H_4(OCO \cdot OC_2H_5)_2 + 2HCl,$$

belongs to this class, and is obtained, in excellent yield, by boiling the constituents, in benzene solution, with calcium carbonate.

All these inorganic neutralizing agents are inferior in their range of application to certain organic bases, such as pyridine. These bases are generally used not only to neutralize the acid, but also to dissolve the reacting substances; the action is, of course, favored by the very fact of these bodies being in solution.

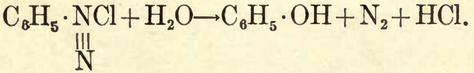
The formation of hydrhaloïd acids also occurs during the direct action of halogens on organic compounds (substitution); in the majority of cases it is unnecessary to deal specially with this by-product, particularly when working with chlorine or bromine. Iodine does not directly replace hydrogen in hydrocarbons, such as benzene, on account of the reducing action of hydriodic acid; in these circumstances an oxidizing agent is added to the reacting materials, the effect of which is to convert the hydrogen iodide into water and iodine, and so allow the substitution to proceed to completion. The substances usually employed for this purpose are lead oxide, mercuric oxide, or potassium iodate; where the oxidation of hydrogen chloride or hydrogen bromide is desired, potassium chlorate or potassium bromate is selected. In certain cases the oxidizing agent may consist of the solvent employed; if this is fuming sulphuric acid, a portion of the dissolved sulphuric anhydride may be reduced. An example is afforded by the preparation of tetrabromoterephthalic acid, by dissolving terephthalic acid in fuming sulphuric acid, adding bromine, and gradually heating up to 200°:

$$C_6H_4(CO\cdot OH)_2 + 4Br + 4SO_3 \rightarrow C_6Br_4(CO\cdot OH)_2 + 2H_2SO_4 + 2SO_2.$$

Sodium acetate is frequently employed for the neutralization of halogen acids when the reaction producing them is carried out in aqueous solution; the acetic acid which is liberated is usually without action on the other substances present. The effects caused by the presence of acids may be still further reduced, if necessary, by using, in place of sodium acetate, the salt of a weaker organic acid.

The same result may, however, be attained by the addition to the solution of an inorganic salt, such as borax or sodium silicate. The acidity of boric acid in solution is practically negligible, and that of silicic acid entirely so; this procedure is of course applicable to reactions other than those involving the use of free halogen.

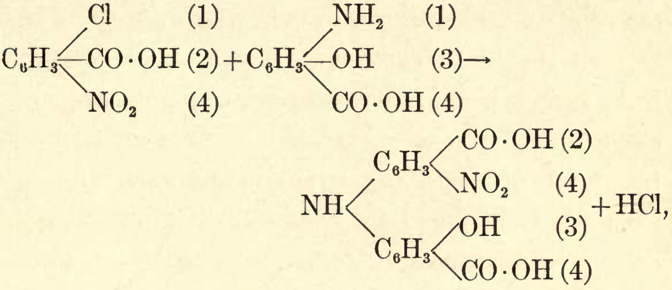
As is well known, diazonium salts are converted into the corresponding phenols by boiling in aqueous solution:



$$C_6H_5\cdot\underset{\underset{N}{|||}}{N}Cl + H_2O \rightarrow C_6H_5\cdot OH + N_2 + HCl.$$

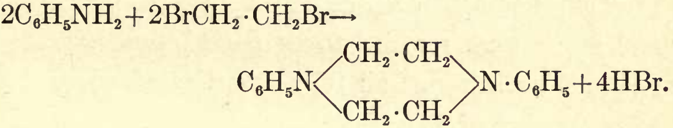
The yield is usually poor, probably because the nascent hydrochloric acid acts as a condensing agent; it may, therefore, be confidently anticipated that, in many cases, the yield would be improved by boiling the diazonium salt in borax solution instead of water.

A number of other inorganic salts, some soluble, others insoluble, may be employed for the absorption of the nascent halogen acid; sodium carbonate is one of these and, as previously stated, calcium carbonate is another; it is used either in the precipitated form or as marble. By the action of chlorine on acetone substitution takes place, but the condensing action of the hydrochloric acid produced causes the formation, in considerable quantity, of the numerous condensation compounds of acetone; moreover, one of these, mesityl oxide, happens to have almost the same boiling-point as chloracetone itself; hence, in spite of many efforts, this latter compound long resisted all attempts to isolate it. In 1893, however, it was directly obtained, in a high degree of purity, with the greatest ease, by adding marble to the acetone before commencing the chlorination; in this case sodium carbonate is obviously unsuitable. Sodium carbonate is employed to neutralize the hydrogen chloride produced by the interaction of chloronitrobenzoic acid, used in the form of its sodium salt, and aminophenol; the analogous action of aminosalicylic acid and paranitrochlorobenzoic acid,



$$C_6H_3\begin{cases}Cl & (1)\\ CO\cdot OH & (2)\\ NO_2 & (4)\end{cases} + C_6H_3\begin{cases}NH_2 & (1)\\ OH & (3)\\ CO\cdot OH & (4)\end{cases} \rightarrow NH\left<\begin{matrix}C_6H_3\left<\begin{matrix}CO\cdot OH & (2)\\ NO_2 & (4)\end{matrix}\right.\\ C_6H_3\left<\begin{matrix}OH & (3)\\ CO\cdot OH & (4)\end{matrix}\right.\end{matrix}\right. + HCl,$$

is carried out by heating the constituents with water and calcium carbonate, during six hours, at 120°. In 1859 diethylenediphenyldiamine was prepared in accordance with the equation



$$2C_6H_5NH_2 + 2BrCH_2\cdot CH_2Br \rightarrow C_6H_5N\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right>N\cdot C_6H_5 + 4HBr.$$

The results, however, were not specially good on account of the acid produced during the reaction; its neutralization, by means of the bases present, always gave rise to the formation of complex mixtures of secondary bases. In 1889 ignited sodium carbonate was employed as neutralizing agent; in consequence of this the yields increased to 80 per cent. of the theoretical, and the formation of tarry substances was avoided. The essential condition for the successful conduct of the reaction is that the medium in which the substances interact should be continuously neutral, or only acid from carbonic acid; hence, in such operations as the alkylation of amino acids the latter are employed in the form of their salts; ethylaminacetic acid, for example, is prepared by heating, under pressure, the calculated quantities of sodium aminoacetate, ethylic chloride, and calcium carbonate:

$$2NH_2\cdot CH_2\cdot CO\cdot ONa + 2C_2H_5Cl + CaCO_3 \rightarrow$$
$$2C_2H_5NH\cdot CH_2\cdot CO\cdot ONa + CaCl_2 + CO_2 + H_2O.$$

The facts detailed above do not of course profess to exhaust what is even already known of the subject, and much work remains to be done before it can be regarded as being at all fully investigated. In many cases fixation of the acid is much more difficult than in the foregoing, as the following example shows. v. Baeyer has proved that the oxidation of ethylic indoxylate to ethylic indoxanthinate is accomplished most conveniently by means of ferric chloride, but the oxidation is one of the most delicate reactions known in the whole indigo group, partly because the hydrochloric acid formed decomposes the ethylic indoxanthinate, partly because the oxidation may cease with the formation of an intermediate compound. These difficulties were overcome by dissolving ethylic indoxylate in four parts of acetone, adding recently precipitated ferric hydroxide, and then ferric chloride, in acetone solution, the temperature being maintained at 60°. The ferric hydroxide not only secures the neutrality of the liquid by combining with the acid, but also regenerates the oxidizing agent.

In the previous pages consideration has been restricted to the neutralization of the inorganic acid while in the nascent state, but it is possible to inhibit the formation of acid by a suitable arrangement of conditions and proper selection of materials. E. Fischer's oxidation of glycerol to glycerose furnishes an example of this; originally the oxidation was accomplished by means of bromine in presence of sodium carbonate:

$$C_3H_8O_3 + Br_2 \rightarrow C_3H_6O_3 + 2HBr.$$

In these circumstances the reaction takes place only with difficulty, but the substitution of lead glyceroxide for the glycerol gave a good yield of almost pure glycerose:

$$C_3H_6O_3Pb + Br_2 \rightarrow C_3H_6O_3 + PbBr_2.$$

Difficulties reciprocal to those hitherto discussed arise from the production of free alkali during the course of a reaction; this occurs, for example, in oxidation by means of neutral potassium permanganate solution:

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O.$$

The difficulty may be obviated by the addition to the solution of magnesium sulphate, which interacts with the potassium hydroxide to form potassium sulphate and magnesium hydroxide, the latter, being insoluble, is necessarily inactive. The oxidation of phenylsemicarbazine to phenylazocarbonamide,

$$C_6H_5NH \cdot NH \cdot CO \cdot NH_2 + O \rightarrow C_6H_5 \cdot N:N \cdot CO \cdot NH_2 + H_2O,$$

is best accomplished by mixing magnesium sulphate, in excess, with the hot aqueous solution of the semicarbazine and gradually adding the necessary amount of saturated solution of potassium permanganate.

It has been previously mentioned that nitrocompounds are reduced to hydroxyl derivatives by means of zinc-dust in presence of ammonium salts; although this is the best method to employ, yet the reduction may be accomplished in other ways, provided the medium in which the action occurs is maintained uniformly neutral. Tertiary isobutylglyceryl $- \beta -$ is hydroxylamine obtained from nitroisobutylglycerol,

$$NO_2 \cdot C(CH_2OH)_3 + 4H \rightarrow HO \cdot NH \cdot C(CH_2 \cdot OH)_3 + H_2O,$$

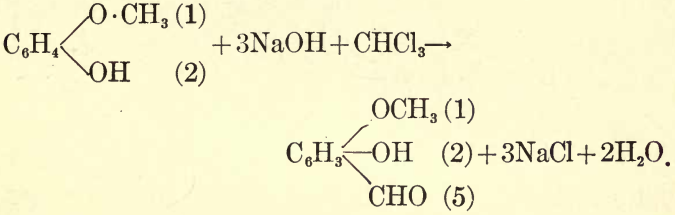
by dissolving it, together with crystallized aluminium sulphate, in a large volume of water and adding sodium amalgam; the sodium hydroxide reacts immediately on its production, and precipitates aluminium hydroxide so that the liquid cannot become alkaline.

The following method for the preparation of nitramino derivatives affords an excellent illustration of the subject-matter of this chapter. Kekulé stated that nitramino compounds can only be obtained from dinitro derivatives if the latter are in solution when acted on by the reducing agent. For example, working with aqueous media, and employing tin and hydrochloric acid, he suggested that the acid dissolved the nitramino compound as it was formed, and that in solution it was much more easily acted upon by stannous chloride than was the insoluble dinitro derivative; hence the second nitro group was reduced before the formation of more nitramino compound. In consequence of this it was customary for many years to carry out such reductions in alcoholic instead of in aqueous solution. The limitations imposed by Kekulé's theory will, however, be maintained if a reducing agent is employed which reacts as readily with the dinitro derivative as with the nitramino compound, or, in other words, the experimental conditions must be such that the latter compound does not become, by passage into solution or in any other way, more sensitive to the reducing agent than the original substance. In 1891 Wülfing showed that nitramino compounds could be prepared without the use of alcohol, provided the reduction was effected by means of iron and hydrochloric acid, sulphuric acid, or acetic acid. Only a very small quantity of acid is necessary when iron is employed; consequently little of the nitramino compound is at any time dissolved, and it is eventually precipitated by the iron as the latter neutralizes the acid. Although the reduction of the solubility of the nitramino compound to a minimum by the use of the least possible quantity of acid is of primary importance for the reaction, the amount of water employed as solvent is almost equally so. The equations

$$-NO_2+2Fe+H_2O \rightarrow -NH_2+Fe_2O_3,$$
$$-NO_2+2Fe+3H_2O \rightarrow -NH_2+Fe_2O(OH)_4,$$

indicate that, by this method of reduction, the quantity of water involved is also relatively little. Provided, then, that care be taken to add it gradually in small portions instead of all at once, all the necessary conditions are realized for a partial reduction to take place, and this is what actually occurs. The preparation of metanitraniline from metadinitrobenzene will serve as an illustration. Metadinitrobenzene is heated at 100° with small quantities of acid and water; iron powder, mixed with a little water, is gradually added, the whole being constantly stirred; the addition of iron is stopped when only a small amount of the dinitrobenzene remains unattacked. After further agitation alkali is added, and the mixture of metanitraniline, dinitrobenzene, and metaphenylenediamine is separated. If the operation has been properly conducted, the production of the last should not exceed 1 per cent.

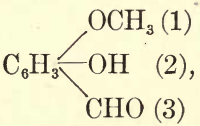
In 1876 Tiemann and Reimer discovered a method for the preparation of aldehydes by the interaction of a phenol, sodium hydroxide, and chloroform; in this manner they synthesized vanillin from guaiacol, in accordance with the equation



$$C_6H_4\left\langle\begin{matrix}O\cdot CH_3\ (1)\\ OH\quad\ (2)\end{matrix}\right. + 3NaOH + CHCl_3 \rightarrow$$

$$C_6H_3\left\langle\begin{matrix}OCH_3\ (1)\\ OH\quad (2)\\ CHO\ \ (5)\end{matrix}\right. + 3NaCl + 2H_2O.$$

The yield at the best did not exceed 5 per cent., and large quantities of tarry matter were formed; consequently many more valuable methods for the technical preparation of vanillin were subsequently worked out by the original discoverers and by others, but the first one can be made to give excellent results provided the conditions of reaction are suitably adjusted so as to facilitate to the greatest possible degree the interaction of the constituents. These conditions were realized by Traub in 1896; it is well known that aldehydes are easily converted into resinous bodies by the action of alkalies; hence it would appear to be undesirable to add the necessary large excess of alkali directly, in one portion, to the mixture of chloroform and phenol; when the alkali was added gradually to the phenol, chloroform, and water, boiling together in a reflux apparatus, better results were obtained, but the production of tarry matter was still considerable. Chloroform and aqueous liquids can of necessity react only slowly; this point was the next to receive attention, and it was found that when alcoholic potassium hydroxide was employed, and the solvent water also replaced by alcohol, the results were admirable. In these circumstances the chloroform reacts far more readily; the operation is therefore completed in a very much shorter time, the resulting liquid is usually barely yellow, seldom more than a shade darker, and the product deposited from it consists almost exclusively of aldehydes free from resin. The maximum quantity of guaiacol which could be transformed in one operation by the first method was 5 grams; the use of more resulted in complete resinification; by the modified process 10 kilograms may be readily operated on at once, and the separation of the vanillin from the small quantity of isomeric compound,



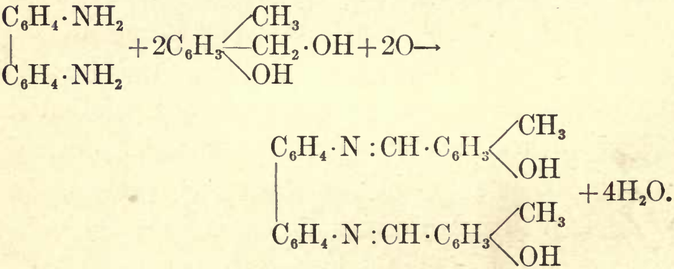
$$C_6H_3\left\langle\begin{array}{ll}OCH_3 & (1)\\ OH & (2),\\ CHO & (3)\end{array}\right.$$

which is simultaneously formed, can be effected with ease.

The preparation of aldehydes is a matter of difficulty, because they so readily undergo transformation during the course of the reaction by which they are formed. A method has been devised to overcome this drawback; it differs entirely from the one just described, because it utilizes the oxidation process for the preparation of aldehydes, and not a specialized reaction; consequently its applicability is extremely general. In principle the method consists in causing the aldehyde, at the moment of its production, to enter into combination with some suitable substance, so that it is protected from spontaneous change and from the further action of the reagents. At present it is customary to attain this result by adding to the materials employed in the reaction such substances as will yield benzylidene or acetyl derivatives of the aldehyde. The oxidation may be effected by means of sulphuric acid and benzidine chromate, instead of sulphuric acid and potassium bichromate. An example is afforded by the preparation of homosalicylic aldehyde from the corresponding alcohol: homosaligenin is mixed, in aqueous solution, with the necessary amount of benzidine chromate,

$$C_{12}H_{12}N_2\cdot H_2CrO_4,$$

and the calculated quantity of sulphuric acid gradually added; the reaction takes place in accordance with the equation

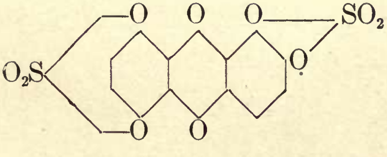


$$\begin{array}{l} C_6H_4\cdot NH_2 \\ | \\ C_6H_4\cdot NH_2 \end{array} + 2C_6H_3\!\left\langle \begin{array}{l} CH_3 \\ CH_2\cdot OH \\ OH \end{array}\right. + 2O \longrightarrow$$

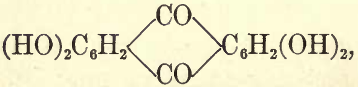
$$\begin{array}{l} C_6H_4\cdot N:CH\cdot C_6H_3\!\left\langle \begin{array}{l} CH_3 \\ OH \end{array}\right. \\ | \\ C_6H_4\cdot N:CH\cdot C_6H_3\!\left\langle \begin{array}{l} CH_3 \\ OH \end{array}\right. \end{array} + 4H_2O.$$

The condensation compound of homosalicylic aldehyde and benzidine is gradually deposited; when boiled with dilute sulphuric acid it is decomposed, and the liberated aldehyde distils over with the steam. The method of procedure followed when acetic anhydride is employed is illustrated by the preparation of isophthalic aldehyde. Acetic anhydride, glacial acetic acid, sulphuric acid, and metaxylene are mixed, cooled, and chromic anhydride gradually added. The completion of the reaction is recognized by the deposition of a solid substance from a portion of the mixture to which water has been added so as to dilute it and decompose the acetic anhydride; the solid consists of isophthalic aldehyde tetracetate; when boiled with dilute hydrochloric acid it yields the aldehyde in a state of purity.

At high temperatures the hydroxyl radicle may become as sensitive as the aldehyde group is at all temperatures, and the need for its protection as great; the hydroxyl derivatives of the anthracene series have been especially well investigated in this connection. In 1890 it was found that at temperatures not exceeding 60° anthracene derivatives were oxidized to hydroxyl compounds by the action of fuming sulphuric acid containing a large percentage of anhydride. As intermediate products sulphuric esters of the hydroxyl derivatives were obtained; thus, from alizarin, the ester

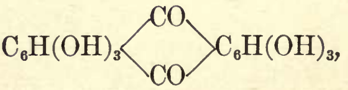


is formed. In many cases, however, these products could not be isolated, owing to the original substance being decomposed in consequence of the disruptive action of the strongly fuming acid. Later it was found that fuming acid was not essential to the oxidation at temperatures above 250°; it could be accomplished by means of concentrated sulphuric acid; the tendency of the hydroxyl derivatives to undergo decomposition is, of course, greatly increased at these elevated temperatures, but it may be entirely overcome by the addition, to the mixture, of some substance capable of esterifying the hydroxyl derivatives immediately they are produced; excellent results have attended the use of boric acid and arsenic acid for this purpose. Tetrahydroxyanthraquinone (anthrachrysol),



$$(\mathrm{HO})_2\mathrm{C}_6\mathrm{H}_2\left<\begin{matrix}\mathrm{CO}\\ \\ \mathrm{CO}\end{matrix}\right>\mathrm{C}_6\mathrm{H}_2(\mathrm{OH})_2,$$

gradually decomposes by the action of concentrated sulphuric acid at high temperatures, but if boric acid is added to the mixture, an excellent yield of hexahydroxyanthraquinone,



$$\mathrm{C}_6\mathrm{H}(\mathrm{OH})_3\left<\begin{matrix}\mathrm{CO}\\ \\ \mathrm{CO}\end{matrix}\right>\mathrm{C}_6\mathrm{H}(\mathrm{OH})_3,$$

is obtained.

It is generally recognized that, in almost all cases, the best method of preparing acid chlorides in a state of purity consists in treating the acid with phosphorus pentachloride, and separating the resulting mixture of acid chloride and phosphorus oxychloride by fractional distillation. The method has, of course, specially commended itself in cases where the mixture of acid chloride and phosphorus oxychloride could be utilized directly for further transformations without previous separation; examples of this have been already given (*vide* p. 17). In 1898 Ashan showed that in certain classes of compounds the yield of final product could be improved, and its preparation rendered easier, if the acid chloride were obtained from phosphorus trichloride, instead of the pentachloride. Ashan's work was chiefly concerned with the preparation of amides from acid chlorides; the transformation of the latter into the former, by means of aqueous ammonia, was first investigated by Liebig and Wöhler in 1832; it involves the isolation of the acid chloride. Fifty years later A. W. Hofmann criticised the method adversely on this account, pointing out that its employment would seldom be advantageous because of the loss of time and material involved in the preparation and purification of the acid chloride. In the same year, 1882, an improvement was introduced by Krafft and Stauffer which consisted in mixing the acid with phosphorus oxychloride, and adding the mixture gradually to the aqueous ammonia. The acids they worked with have high molecular weights, consequently the chlorides can usually be prepared only with considerable difficulty. The chief objection to this method is that the phosphorus oxychloride dehydrates a portion of the amide at the moment of its formation, converting it into the nitrile; this, in itself, decreases the yield, and further loss of substance is sustained during the purification of the amide, as it always retains traces of the nitrile with great tenacity. Another objection to the method is found in the quantity of ammonia required: eight molecules are needed for the decomposition of the mixture of chlorides, but only two molecules are converted into the amide:

$$R\cdot COCl + 2NH_3 \rightarrow R\cdot CO\cdot NH_2 + NH_4Cl;$$
$$POCl_3 + 6NH_3 + 3H_2O \rightarrow PO(ONH_4)_3 + 3NH_4Cl.$$

All these drawbacks are overcome by the use of phosphorus trichloride, instead of the pentachloride, for the conversion of the acid into its chloride; moreover, the conversion is accomplished by means of one atom of chlorine instead of five:

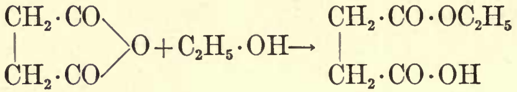
$$3R\cdot CO\cdot OH + PCl_3 \rightarrow 3R\cdot CO\cdot Cl + H_3PO_3.$$

The reaction is completed by gently heating the mixture for a short time. After cooling by means of ice-water, the phosphorus acid, which is formed instead of phosphorus oxychloride, becomes so viscid that it is easy to pour off the mobile acid chloride; the latter is then dropped into aqueous ammonia and furnishes, directly, an excellent yield of amide, free from nitrile and in a high degree of purity.

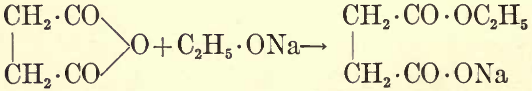
It is now necessary to return to the consideration of sodium ethoxide, which will here be regarded as consisting of ethylic alcohol with its mobile hydrogen atom fixed by means of sodium; this point of view is, therefore, the complement of that elucidated on p. 28. In 1859 Heintz endeavored to prepare ethylic hydrogen succinate by boiling succinic anhydride with absolute alcohol, neutralizing the product with potassium carbonate, and precipitating the ethylic potassium salt,

$$C_2H_5O \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot OK,$$

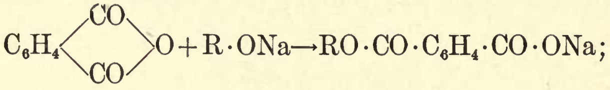
by means of ether; the precipitate, however, could not be induced to solidify, and therefore the method is unreliable because the results are uncertain. In 1893 Brühl, through a careful study of the experimental conditions, was enabled to introduce modifications which rendered the reaction thoroughly trustworthy and gave excellent yields. The production of the ethylic hydrogen salt, which is intermediate between the free acid and the normal ester, by boiling the anhydride of the dibasic acid with alcohol, is eminently calculated to lead to the formation of by-products, because of the uncertainty of determining the end of the reaction. Brühl avoided this difficulty by using sodium ethoxide in place of alcohol; this prevents the production of free acid and gives, directly, the sodium ethylic salt in which, of course, the mobile hydroxyl of the second carboxyl group is fixed from the moment of its formation. In the case of succinic acid the two reactions are represented by the equations



and



The above reaction not only applies to succinic anhydride and sodium ethoxide, but also to other metallic alkyloxides derived from alcohols of the most complex constitution; indeed the process furnishes one of the best methods for the isolation of such alcohols from complicated mixtures. Alcohols of the terpene series, for example, such as linalool or geraniol, which occur in admixture with a variety of substances, are conveniently separated by treatment with sodium; to the product is then added ether and phthalic anhydride, which results in the formation of a sodium alkylic phthalate,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + R\cdot ONa \rightarrow RO\cdot CO\cdot C_6H_4\cdot CO\cdot ONa;$$

this compound may be separated by the addition of water, in which the impurities do not dissolve, or it may be extracted from the aqueous solution by means of ether. The sodium alkylic phthalate, after isolation, is readily hydrolyzed by the action of alcoholic potassium hydroxide, during several hours, at the ordinary temperature; by this means the terpene alcohol is obtained in a high degree of purity.

The latest method for the preparation of fuchsin forms an admirable illustration of the excellent results which may follow from modified experimental conditions introduced into complex processes as the result of a clear, wide-reaching view of the theoretical conditions. Since the early sixties fuchsin has been prepared by the oxidation of a mixture of aniline and toluidine as represented by the equation

$$CH_3\cdot C_6H_4\cdot NH_2 + 2C_6H_5\cdot NH_2 + 3O \rightarrow HO\cdot C(C_6H_4NH_2)_3 + 2H_2O.$$

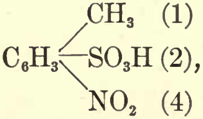
The most convenient oxidizing agent proved to be arsenic acid, but its use caused the dye to be poisonous;

consequently the manufacture, in the seventies, of non-toxic fuchsin, by the use of nitrobenzene as the oxidizing agent, constituted a most important technical advance. Considered from the chemical standpoint neither method was specially good because neither gave a yield exceeding 38 per cent. As the result of much brilliant and strenuous work, participated in by many of the leading chemists of the time, fuchsin was finally shown to be a triphenylmethane derivative, but the establishment of this fact did not lead to any immediate change in the method of its manufacture, and it was not until 1891 that the poor yield was recognized as being due to *overstrain of the reaction*, as it may be termed. In the old fuchsin fusion the methane carbon atom, which linked the triphenyl complex, had to be derived from the paratoluidine, which itself possesses a fairly complicated molecular structure. The production of this carbon atom was necessarily accompanied by a considerable variety of decomposition phenomena, and consequently to the formation of many by-products. The addition of sodium methylic sulphate to the ordinary ingredients of the fuchsin fusion makes it possible to obtain the necessary methane carbon atom from one of the simplest derivatives of methane, instead of by the decomposition of a complex compound, and this of course facilitates the participation of that carbon atom in the reaction which, in consequence of these new conditions, proceeds with facility, the formation of by-products being reduced to a minimum. The simplification may, however, proceed further; the paratoluidine is obviously unnecessary, and the aniline may also be dispensed with; the formation of the desired triphenylmethane derivative is fully secured by the use of a mixture of orthotoluidine, sodium methylic sulphate, and arsenic acid, which, moreover, yields pure triaminorthotolyl carbinol, the most valuable fuchsin dye. It is even possible to secure a further advantage. Methylic alcohol volatilizes at too low a temperature to admit of its carbon atom entering into the reaction; the employment of its derivative, sodium methylic sulphate, allows the operation to be performed in an open vessel at a temperature sufficiently high to enable the methyl group to participate in the change. The use of an autoclave readily overcomes this difficulty, and permits the sodium methylic sulphate to be dispensed with, consequently fuchsin is now manufactured by heating orthotoluidine with methylic alcohol and arsenic acid, at 160°, in acordance with the equation

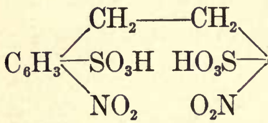
$$HO\cdot CH_3 + 3\overset{1}{C}H_3\cdot C_6H_4\overset{2}{N}H_2 + 3O \rightarrow HO\cdot C(C_6H_3\overset{1}{C}H_3\cdot \overset{2}{N}H_2)_3 + 3H_2O.$$

These changes have not only rendered the process one of the most simple conceivable, but have caused the yield to become almost quantitative.

In connection with the reference made above to the use of nitrobenzene as an oxidizing agent it may be stated that, in the author's opinion, "overstrain of the reaction" will always accompany the employment of any nitroderivative for this purpose, no matter whether it be employed for extramolecular or intramolecular oxidation; the decomposition which must precede the production of oxygen necessarily involves the formation of substances which are well suited to cause resinification of the compounds which it is desired to prepare. Thus, when warmed with alkalies, paranitrotoluenesulphonic acid,

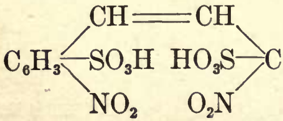


is converted into dinitrodibenzyldisulphonic acid,



[CH_2; SO_3H; NO_2=1;2;4,]

or into dinitrostilbenedisulphonic acid,



CH; SO_3H; [NO_2=1; 2; 4,]

the oxygen necessary for the oxidation of the methyl groups being furnished by the nitro groups of other molecules of the original compound. The yield of the two products is extremely poor, but a vast improvement in this respect is effected if sodium nitrotoluenesulphonate, in aqueous solution, is oxidized by means of quantities of sodium hypochlorite solution calculated for the respective products.

Skraup's admirable synthesis of quinoline, discovered in 1880, may now be considered from this point of view. To the original mixture of aniline, glycerol, and sulphuric acid, nitrobenzene was added in the hope that the excess of hydrogen, produced in accordance with the equation

$$C_6H_5 \cdot NH_2 + C_8H_8O_3 \rightarrow C_9H_7N + 3H_2O + H_2,$$

would combine with some of the oxygen of the nitrobenzene and so improve the yield. The equation

$$C_6H_5NH_2 + 2C_3H_8O_3 + C_6H_5NO_2 \rightarrow 2C_9H_7N + 7H_2O + O$$

shows an excess of oxygen which, by its action on the substances present, must reduce the yield; after many experiments it was found possible to increase the amount of quinoline formed to about 70 per cent., but not more than this could be obtained although, if the materials are taken in the proportion

$$2C_6H_5 \cdot NH_2 + 3C_3H_8O_3 + C_6H_5 \cdot NO_2 \rightarrow 3C_9H_7N + 11H_2O,$$

neither oxygen nor hydrogen is in excess. In 1896 Knüppel substituted the nitrobenzene by arsenic acid, which, of course, cannot form tarry matters by its reduction. He obtained without difficulty a 92 per cent. yield of quinoline, in accordance with the equation

$$2C_6H_5NH_2 + 2C_3H_8O_3 + 2H_3AsO_4 \rightarrow 2C_9H_7N + 11H_2O + As_2O_3.$$

The preparation of nitroquinolines by Skraup's original method is necessarily attended by very poor yields because, in the conversion of the nitranilines, the nitro groups take part in the reaction instead of passing intact into the quinoline molecule. In these cases, too, arsenic acid has proved to be an excellent oxidizing agent, and by its use the yield of orthonitroquinoline, for example, is 57 per cent. of the theoretical.

In concluding this chapter attention may be directed to the nitrating action which nitrous acid occasionally exhibits. It forms an excellent agent for the nitration of the three hydroxybenzoic acids, and for the alizarinsulphonic acids. This action can obviously only occur in consequence of the oxidation, during the course of the reaction, of a portion of the nitrous acid to nitric acid in some such manner as indicated by the equation

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

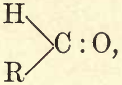
This appears to indicate an "overstrain of the reaction" which would, of necessity, involve either a diminution in the yield of the nitro-derivative, or a reduction in the apparent efficiency of nitrous acid as a nitrating agent. The author therefore suggests that nitration by means of the usual mixture of nitrite and sulphuric acid will, in many cases, be greatly facilitated by the addition of arsenic acid, or some similar agent, which will render superfluous the oxidation of one portion of the nitrous acid by means of another; this method of nitration permits of the use of nitric acid in a nascent state entirely different from that involved in its liberation from a mixture of potassium nitrate and sulphuric acid.

CHAPTER IV.

INFLUENCE OF NEIGHBORING ATOMS AND ATOMIC COMPLEXES.

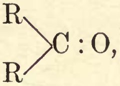
THE mutual influence of neighboring atoms and atomic complexes, in both the aliphatic and aromatic series of compounds, is a well-known phenomenon, but its application to practical work has frequently failed to receive the recognition which its value demands. In the case of aromatic compounds its application for the facilitation of reactions, and for the improvement of yields, is assuredly capable of far wider extension than it has hitherto been accorded. It is well known that many atoms, especially those of the halogens, and many atomic complexes, such as hydroxyl, are far more reactive in aliphatic than in aromatic compounds, but this is not universally true: it fails to apply if the atoms or groups in question are rendered mobile by the influence of neighboring atoms or groups present in the aromatic compound. In the case of the halogens a recently discovered example, given subsequently, demonstrates this proposition in the clearest possible manner.

In the aliphatic series of compounds the subject may be illustrated by considering the influence exerted on an oxygen atom, doubly linked to carbon, by other atoms linked to the same carbon atom. The divalent carbonyl group may be linked to a hydrogen atom and a hydrocarbon radicle,



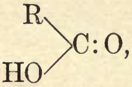
$$\left.\begin{matrix}H\\R\end{matrix}\right>C:O,$$

or to two hydrocarbon radicles,



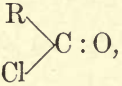
$$\left.\begin{matrix}R\\R\end{matrix}\right>C:O,$$

forming, therefore, aldehydes and ketones respectively; by the action of phosphorus pentachloride on each of these classes of compounds two atoms of chlorine may be substituted for the oxygen atom. Combination of carbonyl with hydroxyl gives the carboxyl group, which, together with a hydrocarbon radicle, yields the complex



$$\left.\begin{matrix}R\\HO\end{matrix}\right>C:O,$$

characteristic of organic acids; phosphorus pentachloride is without action on the doubly linked oxygen atom of these compounds, but it causes substitution of the hydroxyl by one atom of chlorine. The resulting compounds are termed acid chlorides,



$$\begin{matrix} R \\ Cl \end{matrix} \!\!>\!\! C : O,$$

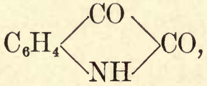
and the above fact may be expressed by saying that the chlorine atom present in them exerts a very strongly protective influence on the oxygen atom against the attack of the phosphorus pentachloride. Replacement of the chlorine atom by the cyano or amino radicles produces a complete change; the resulting compounds behave like aldehydes or ketones, and, by the action of phosphorus pentachloride, readily exchange oxygen for two chlorine atoms. It is possible, therefore, by this circuitous method, to increase the mobility, and hence the reactivity, of the doubly linked oxygen atom of a carboxyl group, and consequently to realize such transformations as the conversion of ethylic oxamate (oxamethane)

$$H_2N \cdot CO \cdot CO \cdot OC_2 \cdot H_5,$$

into ethylic dichloraminoacetate,

$$H_2N \cdot CCl_2 \cdot CO \cdot OC_2H_5.$$

In the course of his work on the synthesis of indigo v. Baeyer utilized the preceding observations to effect the reduction of isatin. The direct interaction of pseudoisatin,



$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO,$$

and any reducing agent is exclusively confined to that carbonyl group which is in closest proximity to the benzene nucleus; if, however, the pseudoisatin is treated with phosphorus pentachloride, and the resulting dichloro derivative reduced, the carboxyl group directly linked to imide is affected.

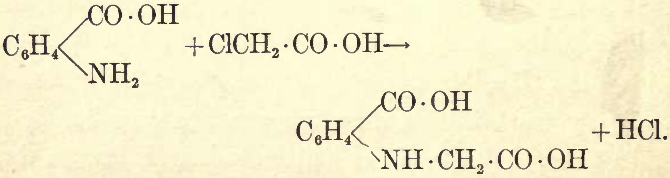
Koepp states that acid amides, in which the aminic hydrogen is fixed, are reduced by contact of their aqueous solutions with zinc-dust, during twenty-four hours, at 50°; in this manner he obtained zinc phenylaminoacetate (phenyl glycocoll),

$$C_6H_5\cdot NH\cdot CH_2\cdot CO\cdot OH,$$

from phenylaminoxalic acid,

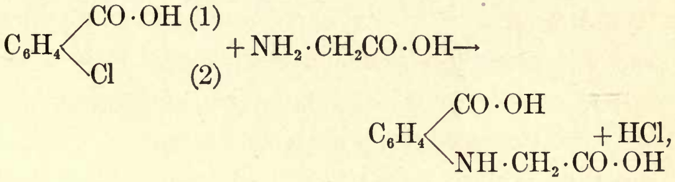
$$C_6H_5\cdot NH\cdot CO\cdot CO\cdot OH.$$

The mutual influence of neighboring atomic groups is far more complicated in the case of cyclic compounds than in that of open chain derivatives, and the subject has hardly received any investigation; consequently work in this direction consists very largely of blind empirical efforts. So little, indeed, is known that processes are still employed which are antiquated and based on wholly insufficient knowledge and which, consequently, not infrequently lead to undesirable results. It is tolerably well established that nitro groups are rendered more mobile and reactive by the presence, in the same ring, of halogen atoms; but until very recently this was not known to be equally true for the carboxyl group, yet the knowledge, had it been available, would have saved an enormous amount of valuable effort, energy, and time. In the preceding pages reference has frequently been made to phenylglycinecarboxylic acid, which is of such great importance for the preparation of synthetic indigo; no attempt has been made to mention all the known methods for its preparation; only those were cited which were specially illustrative of the topics discussed in this volume and which were the result of much brilliant and valuable work. The methods of preparation may be summarized by saying that they effect the substitution, by means of the acetic acid radicle, of an animo hydrogen atom in orthaminobenzoic acid, in accordance with the equation



$$C_6H_4{<}\begin{matrix}CO\cdot OH\\ NH_2\end{matrix} + ClCH_2\cdot CO\cdot OH \rightarrow C_6H_4{<}\begin{matrix}CO\cdot OH\\ NH\cdot CH_2\cdot CO\cdot OH\end{matrix} + HCl.$$

The most widely varying means have been utilized to realize this substitution. The complementary reaction,



$$\mathrm{C_6H_4}\begin{cases}\mathrm{CO\cdot OH}\ (1)\\ \mathrm{Cl}\qquad\quad (2)\end{cases} + \mathrm{NH_2\cdot CH_2CO\cdot OH} \rightarrow \mathrm{C_6H_4}\begin{cases}\mathrm{CO\cdot OH}\\ \mathrm{NH\cdot CH_2\cdot CO\cdot OH}\end{cases} + \mathrm{HCl},$$

would appear, on first consideration, to be simpler and therefore preferable. Moreover, the materials required, viz., orthochlorobenzoic acid and amino-acetic acid, are more readily accessible than those employed in the former reaction, and the fact that the amino group is initially in the acetic acid molecule and not in the ring is also a simplifying factor. In spite of these advantages the practical application of the reaction has only been made within the past two years, because the views which prevailed previously did not justify the expectation that the chlorine atom in the benzene ring would be rendered sufficiently reactive by the presence of carboxyl in the ortho position to it. Experiment shows that the reaction proceeds quantitatively if the two acids, in the form of alkali salts, are mixed in aqueous solution with potassium carbonate and copper turnings, and the liquid boiled during several hours. This single example indicates what startling and valuable results may be expected to be attained by the utilization of the mutual action of neighboring atoms when the subject has been thoroughly and systematically investigated.

In the preceding reaction the copper cannot be regarded as belonging to the group of halogen-carriers, which act chemically; its influence appears to be due solely to "contact action." In the future substances belonging to this class will doubtless become of increasing importance for organic reactions. In the indigo synthesis two of them already occupy a position of the first rank: the one is copper, as has just been stated; the other is mercury, the presence of which is essential to the successful oxidation of naphthalene to phthalic acid by means of sulphuric acid. To this might be added the successful reoxidation, by the influence of platinized asbestos, of the sulphur dioxide produced during the formation of the phthalic acid. Another instance of such action is the employment of iron in Coupier's process for the production of fuchsin. The employment of silica to promote reaction between immiscible substances is frequently attended by the best results; the action appears to be due to its absorbtive power. In consequence of this the surface on which the substances may come into contact is enormously increased. As previously mentioned (p. 38), benzene and sulphuric acid in presence of silica react quantita-

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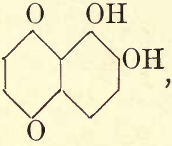
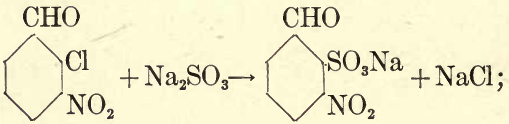
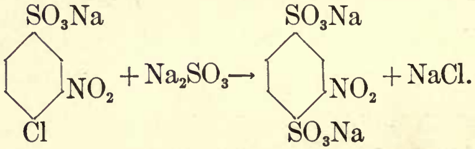
tively, at the ordinary temperature, to form phenylsulphonic acid. Silica (infusorial earth) is also capable of promoting oxidations of a special nature in the case of certain compounds containing nitro groups; thus, orthodinitronaphthalene when treated on the water-bath with feebly fuming sulphuric acid and infusorial earth is not sulphonated, as would naturally be expected, but undergoes conversion into naphthazarol,



the nitro groups being eliminated; the yield is excellent.

A number of other cases showing the influence of neighboring atoms may now be considered; of all compounds which exhibit this property those containing one or more nitro groups possess a special interest, because the influence of that group on neighboring atoms or atomic complexes is utilized, in the Sandmeyer-Gattermann reaction, to effect, *via* the amino group, substitution by means of hydrogen or radicles of all kinds. In many such compounds the nitro groups themselves are more mobile than is generally assumed; they may not only equal, but even exceed, their neighboring halogen atoms in this respect, as shown by their more ready substitution. In such reactions the effect of position isomerism is, of course, very marked. Ortho- and parachloronitrobenzene yield the corresponding nitranilines when heated under pressure with alcoholic ammonia (p. 9); metachloronitrobenzene does not react in this manner. The presence of more substituents, which need not necessarily be nitro groups, increases the mobility of the chlorine atom in orthochloronitrobenzene, as exhibited in the following equations:

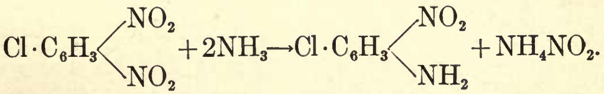




The first reaction occurs by heating the mixture under pressure, the second by boiling in a reflux apparatus. In dinitrochlorobenzene the mobility of the halogen atom is the same as in aliphatic compounds. In consequence of the readiness with which derivatives of this substance crystallize it is employed for the purification of compounds; thus, for example, an acid may be freed from foreign bodies by dissolving the crude material in alcohol, or some other appropriate solvent, adding the calculated quantity of sodium ethoxide, and then alcoholic solution of dinitrochlorobenzene; the resulting dinitrophenylic salt of the acid can be readily removed in a crystalline form. Mono-α-dinitrophenylglycerol ether,

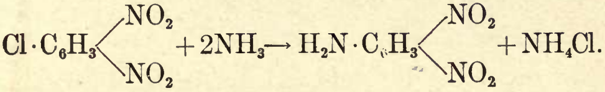
$$C_6H_3(NO_2)_2\cdot O\cdot C_3H_5(OH)_2,$$

is obtained by dissolving the chloride in glycerol, and adding the calculated quantity of alkali in glycerol solution. Trinitrochlorobenzene is also quite reactive; for example, with sodium sulphite it yields sodium trinitrophenylsulphonate. An instance of the nitro group exhibiting a greater mobility than its neighboring halogen atom is furnished by the interaction of saturated alcoholic ammonia and dinitrochlorobenzene; after remaining at the ordinary temperature during four days a nitro group is replaced by an amino radicle, nitrochloraminobenzene being formed, thus:



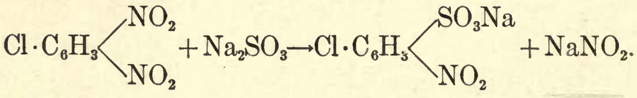
$$Cl\cdot C_6H_3\left\langle\begin{array}{l}NO_2\\NO_2\end{array}\right. + 2NH_3 \rightarrow Cl\cdot C_6H_3\left\langle\begin{array}{l}NO_2\\NH_2\end{array}\right. + NH_4NO_2.$$

If, however, the reaction is allowed to proceed at a higher temperature, under pressure, the halogen atom is replaced, dinitroaminobenzene being formed:



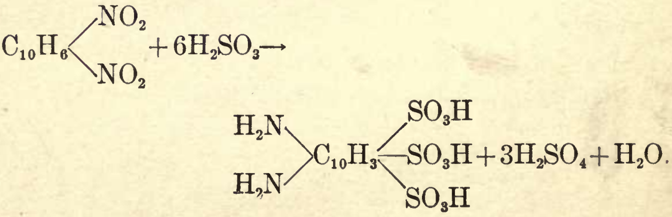
$$Cl\cdot C_6H_3\left\langle\begin{array}{l}NO_2\\NO_2\end{array}\right. + 2NH_3 \rightarrow H_2N\cdot C_6H_3\left\langle\begin{array}{l}NO_2\\NO_2\end{array}\right. + NH_4Cl.$$

Prolonged boiling of dinitrochlorobenzene with sodium sulphite solution likewise causes substitution of a nitro group and not of the chlorine atom, sodium nitrochlorophenylsulphonate being formed:



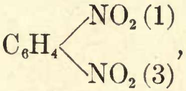
$$Cl\cdot C_6H_3{<}\begin{matrix}NO_2\\ NO_2\end{matrix}+Na_2SO_3\rightarrow Cl\cdot C_6H_3{<}\begin{matrix}SO_3Na\\ NO_2\end{matrix}+NaNO_2.$$

As would naturally be expected, the action of sodium sulphite on nitro derivatives may easily lead to more or less reduction of the nitro groups; this is found to be accompanied by a marked increase in the mobility of the neighboring hydrogen atoms, a result which could not be foreseen. For example, the action of sodium hydrogen sulphite solution on α_1-α_2-dinitronaphthalene not only involves the reduction of the nitro to the amino groups, but also the substitution of three hydrogen atoms by sulphonic radicles, the product obtained being, therefore, diaminonaphthalenetrisulphonic acid:



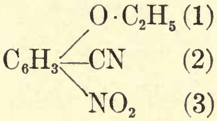
$$C_{10}H_6{<}\begin{matrix}NO_2\\ NO_2\end{matrix}+6H_2SO_3\rightarrow \begin{matrix}H_2N\\ H_2N\end{matrix}{>}C_{10}H_3{\lt}\begin{matrix}SO_3H\\ SO_3H\\ SO_3H\end{matrix}+3H_2SO_4+H_2O.$$

This great mobility of hydrogen atoms may, however, occur in the presence of nitro groups without reduction; thus metadinitrobenzene,



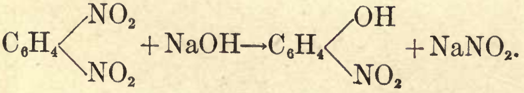
$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ NO_2\ (3)\end{matrix}\right.,$$

is converted into the compound



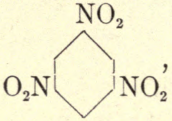
$$C_6H_3\left\langle\begin{matrix}O\cdot C_2H_5 & (1)\\ CN & (2)\\ NO_2 & (3)\end{matrix}\right.$$

by the action of potassium cyanide in alcoholic solution; there occurs the simultaneous substitution of a nitro group by ethoxyl, and of hydrogen by the cyanogen radicle. In compounds containing several nitro groups one of them may be highly reactive without any apparent influence being exercised on the others or on the neighboring hydrogen atoms; thus orthodinitrobenzene yields orthonitrophenol when boiled with aqueous sodium hydroxide:

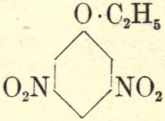


$$C_6H_4\left\langle\begin{matrix}NO_2\\ NO_2\end{matrix}\right. + NaOH \rightarrow C_6H_4\left\langle\begin{matrix}OH\\ NO_2\end{matrix}\right. + NaNO_2.$$

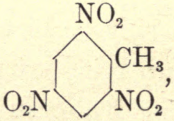
When heated with ammonia the dinitro compound yields orthonitraniline, as previously stated, but pyrocatechol or metaphenylenediamine cannot be obtained by these methods. *s*-Trinitrobenzene,



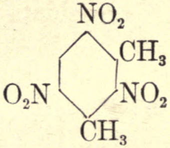
behaves in a similar manner under the influence of sodium ethoxide; only one ethoxy group is introduced, the compound



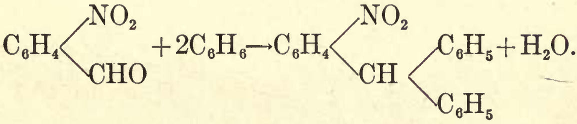
being formed. This reaction does not occur with the homologous compounds symmetrical trinitrotoluene,



and trinitroxylene,



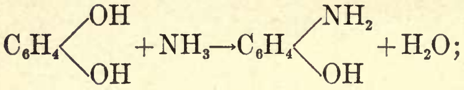
(*vide* p. 92). In many other directions nitro compounds exhibit a much higher degree of reactivity than the non-nitrated substances from which they are derived; it is scarcely possible to obtain any phenol by the direct oxidation of benzene, but by the action of feeble oxidizing agents trinitrobenzene is readily converted into trinitrophenol (picric acid); toluene is also much more difficult to oxidize than nitrotoluene. Similar conditions are found to apply to reactions involving condensation; thus benzene and benzaldehyde do not interact in presence of concentrated sulphuric acid, but, under the same conditions, paranitrobenzaldehyde yields nitrotriphenylmethane:



$$C_6H_4\left\langle\begin{array}{l}NO_2\\CHO\end{array}\right. + 2C_6H_6 \rightarrow C_6H_4\left\langle\begin{array}{l}NO_2\\CH\left\langle\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right.\end{array}\right. + H_2O.$$

The high degree of mobility exhibited by neighboring hydrogen atoms is not specifically induced by nitro groups, as might almost be supposed from the preceding paragraphs. Similar results are produced by the presence of the sulphonic radicle. The preparation of picric acid affords the best known example of this; by the direct action of nitric acid on phenol the yield of picric acid is, at the most, 120–130 per cent., but this is increased to 150–155 per cent. if, previous to nitration, the phenol is sulphonated; moreover, just as the presence of sulphonic radicles facilitates the entry into the molecule of nitro groups, so the presence of these renders the elimination of the sulphonic radicles a matter of great ease; indeed it is effected by boiling with dilute acid in an open vessel.

The remarks made above about polynitro-derivatives apply also to the corresponding hydroxyl compounds; i.e., reactions which occur incompletely or not at all in the case of compounds containing one of these groups may proceed with great facility with substances containing two or more, because their mutual action increases their mobility. Phloroglucinol and rescorcinol react readily with ammonia to form aminophenols:



$$C_6H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + NH_3 \rightarrow C_6H_4\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + H_2O;$$

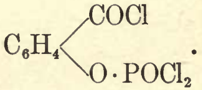
the corresponding reaction with phenol is well known to be very incomplete, otherwise it would constitute the best method for the preparation of aniline. Reactions which do not occur in compounds containing one ring may, however, take place with facility in the case of di- or polycyclic systems; accordingly the method just given affords the best means for the production of α- and β-naphthylamine:

$$C_{10}H_7OH + NH_3 \rightarrow C_{10}H_7NH_2 + H_2O.$$

An example of the high degree of mobility exhibited by halogen atoms under the influence of neighboring groups, when they are present in systems consisting of three rings, is afforded by dichlorotetrahydroxyanthraquinonedisulphonic acid (dichloroanthrachrysonedisulphonic acid), which substitutes its chlorine atoms for the radicles of amines, aminophenols, diamines, etc., if the amine is warmed on the water-bath with the sodium salt of the disulphonic acid, in aqueous solution.

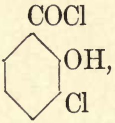
It will be readily seen from the foregoing what an enormous field is open for investigation along the lines which have been indicated, and of what great importance and value the results will be to subsequent workers. Moreover, the development of the subject will ultimately necessitate regard being paid to the methods of modifying reactions; thus, to take an obvious example, a consideration of the reactivity of dinitrochlorobenzene will involve the investigation of the behavior of dinitrochloronaphthalene, dinitrobromobenzene and dinitroiodobenzene.

In the preceding sections consideration has been limited to cyclic compounds containing atoms or radicles which initiate or increase the reactivity of neighboring hydrogen or halogen atoms or of atomic groups. Such induced influence on reactivity may, however, be the exact antithesis of the foregoing, and may be exerted so as to hinder or entirely inhibit a reaction which might otherwise be expected to take place. In the latter cases, as in the former, position isomerism plays an important part. This phenomenon may be appropriately designated the "protective action" of neighboring atoms and groups. One example has been already given (p. 88) in which the protective action of the methyl group inhibits the interaction of sodium ethoxide and trinitrotoluene or trinitroxylene, but with trinitrobenzene the change easily takes place. It is obvious that phenolcarboxylic chlorides could not be expected to be produced by the action of phosphorus pentachloride on the three hydroxybenzoic acids; investigation of the reaction shows that the carboxylic hydroxyl is first attacked, the resulting phosphorus oxychloride then interacts with the phenolic hydroxyl, the final product being a phosphorus oxychloride derivative of phenolcarboxylic chloride,

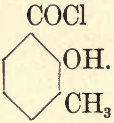


$$C_6H_4\left\langle\begin{matrix}COCl\\ O\cdot POCl_2\end{matrix}\right. .$$

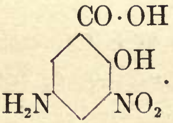
This is consistently true of meta- and parahydroxybenzoic acids and their derivatives, but the phenolic hydroxyl of orthohydroxybenzoic acid (salicylic acid) may be protected against the phosphorus oxychloride by the introduction of halogens, methyl, the nitro group, etc., into the second ortho position relative to this hydroxyl. In these derivatives the phosphorus pentachloride yields only the acid chlorides, such as chlorosalicylic chloride,



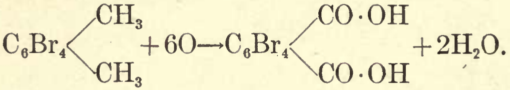
or methylsalicylic chloride,



Similar conditions are found to exist in the naphthalene series of compounds. A further instance of the protection of a phenolic hydroxyl, and also of an amino group in the para position, is afforded by the behavior of paraminophenol towards nitric acid; irrespective of variation in the conditions, the compound is never nitrated, but only oxidized to quinone. In contrast to this the orthocarboxylic acid of the compound, i.e., paraminosalicylic acid, is quantitatively converted, by means of nitric acid, into the nitro derivative



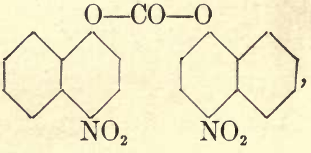
The accumulation of halogen atoms in a cyclic compound appears to protect the ring from disruption, as shown by the following example: Tetrabromoparaxylene can only be converted into tetrabromoterephthalic acid, to a very limited extent, by any of the ordinary oxidizing agents:



$$\mathrm{C_6Br_4}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right. + 6\mathrm{O} \rightarrow \mathrm{C_6Br_4}\left\langle\begin{matrix}\mathrm{CO\cdot OH}\\ \mathrm{CO\cdot OH}\end{matrix}\right. + 2\mathrm{H_2O}.$$

The change can, however, be accomplished by the action of a mixture of nitric acid and potassium permanganate, in large excess, at 180°, under pressure; it cannot be doubted that, under these conditions, paraxylene itself would suffer complete decomposition.

The protective action of an atomic complex may be so great that a nitro group attached to it may be rendered completely unreducible. This is shown in the case of nitro-α-naphthylcarbonate,



and a number of other examples are also known.

At present the number of definitely ascertained instances of protective action is somewhat limited; reactions inhibited from this cause have usually failed to be recorded on account of their negative result.

It is well known that certain acids are not esterified by means of a mixture of alcohol and sulphuric acid or hydrochloric acid, and that certain nitriles and amides are not hydrolyzed by the action of dilute acids. The inhibition of the reaction in these and similar cases is due, apparently, solely to stereomeric influence and consequently does not call for consideration here.

INDEX.

A

PAGE

Acid chlorides, preparation 65, 78, 92
Acids, inhibition of formation 55
  modification of 37
  neutralization .... 48 *et seq.*
Acylanilines 4, 8
Acylation .... 42, 48 *et seq.*
Aldehyde group 77
Aldehydes, preparation 59, 61
Alkali, formation 55
  fusion with 32
  modification of .... 28 *et seq.*
  neutralization 56
Alkylation 46, 54
Amalgams 24
Amines, nitration 4
Amino hydrogen 3
Ammonium derivatives as reagents 34
  salts " " 25
Aniline, nitration .... 3 *et seq.*
Arsenic acid 64, 69
Ashan 65

B

v. Baeyer 79
Bases, inorganic, uses .... 48 *et seq.*

PAGE

Bases, modification of 35
 organic, uses 50, 61
Baubigny 16
Boric acid 51, 64
Brühl 67

C

Carboxyl group 15, 77
Chavanne 16
Chloro derivatives, formation 40
Conditions of reaction, improvement in .... 48 *et seq.*
Contact action 82
Coupier 82

D

Dehydration 39
Diazotizing 44, 83
Dolhard 20

F

Ferric chloride, uses 43, 54
Fischer, E 55
Fixation of labile hydrogen atoms .... 2 *et seq.*
 by hyacyl groups 4
 alkyl " 12
 halogens 20
Fuchsin, preparation .... 61 *et seq.*
Fusion with alkali 32

G

Gattermann 83
Grothmann 16

H

Halogen carriers 82
 derivatives .... 45, 76, 85 *et seq.*, 90

PAGE

Halogens, modification of........ 44
    oxidizing action........ 12
Haloïd acids, formation........ 48, 50
    uses........ 41
Heintz........ 67
Hofmann, A. W......... 65
Hydrochloric acid, formation........ 48 *et seq.*
Hydrogen atoms, fixation........ 2, 4, 12, 20
    reactivity........ 87
Hydrolysis........ 31
Hydrolytic agents........ 29 *et seq.*
Hydroxyl groups........ 13 *et seq.*, 28, 63, 76, 77, 90
    in carboxyl........ 15, 92
    phenols........ 20

I

Indigo, synthesis........ 11, 16, 32, 80
Introductory........ 1

K

Kekulé........ 57
Ketone group........ 77
Knüppel........ 74
Koepp........ 79
Kolbe........ 32
Krafft........ 39, 65

L

Labile hydrogen atoms, fixation........ 2 *et seq.*
Lellmann........ 16
Liebig........ 65

M

Mauthner........ 11
Modification of reactions........ 23 *et seq.*

N

PAGE

Naphthylsulphonic acid, uses.... 39

Neighboring atoms and atomic complexes, influence.... 76 *et seq.*

Nitramines, formation.... 57

Nitranilines.... 3 *et seq.*

Nitration.... 3 *et seq.*, 48, 74, 89

Nitrites, uses.... 44, 74

Nitrobenzene as oxidizing agent.... 72

Nitrous acid as nitrating " 74

O

Organic acids, uses.... 40

  bases, " 35

Orthonitraniline, preparation.... 4 *et seq.*

Oxalic acid.... 6

Oxidizing agents.... 33, 50, 63, 69, 72, 89, 93, 94

Overstrain of reactions.... 70 *et seq.*

P

Paranitraniline, preparation.... 7

Phenols.... 20

Phenylglycinecarboxylic acid.... 11, 12, 32, 80

  sulphonic acid, preparation.... 38, 82

    uses.... 39

Position isomerism, influence.... 18

Potassium as reagent.... 23

  compounds.... 24, 32

Protective action.... 92, 94

Q

Quinoline synthesis.... 73

R

Reactions, modifications of.... 23 *et seq.*

  overstrain of.... 70 *et seq.*

Reduction.... 25, 56

PAGE
Reimer 59
Roos 39

S

Salts, formation 67
    uses 15, 42, 51, 81
Sandmeyer 83
Silica, uses 38, 82
Skraup 63
Sodium as reagent 23
    compounds 28
    ethoxide 28, 29, 67
Stauffer 65
Stereomeric influence 95
Suida 11

T

Tiemann 59
Thio-acids, uses 41
Traub 60

V

Vanillin, preparation 59

W

Wöhler 65
Wulfing 58

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